

Advanced Method for Measurement of the Solid Carbonaceous (Soot) Component of Mobile Source Particulate Matter

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Development Support by California Air Resources Board
Innovative Clean Air Technology (ICAT) Grant 06-03

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Spray Diagnostics

Particulate Emissions

Cloud Research

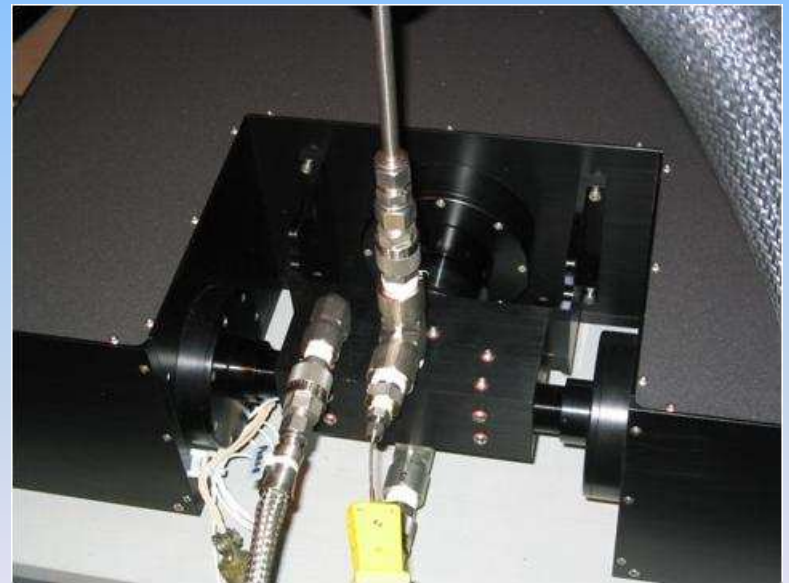
Air Quality/Health

Improvements have significant benefits



Outline

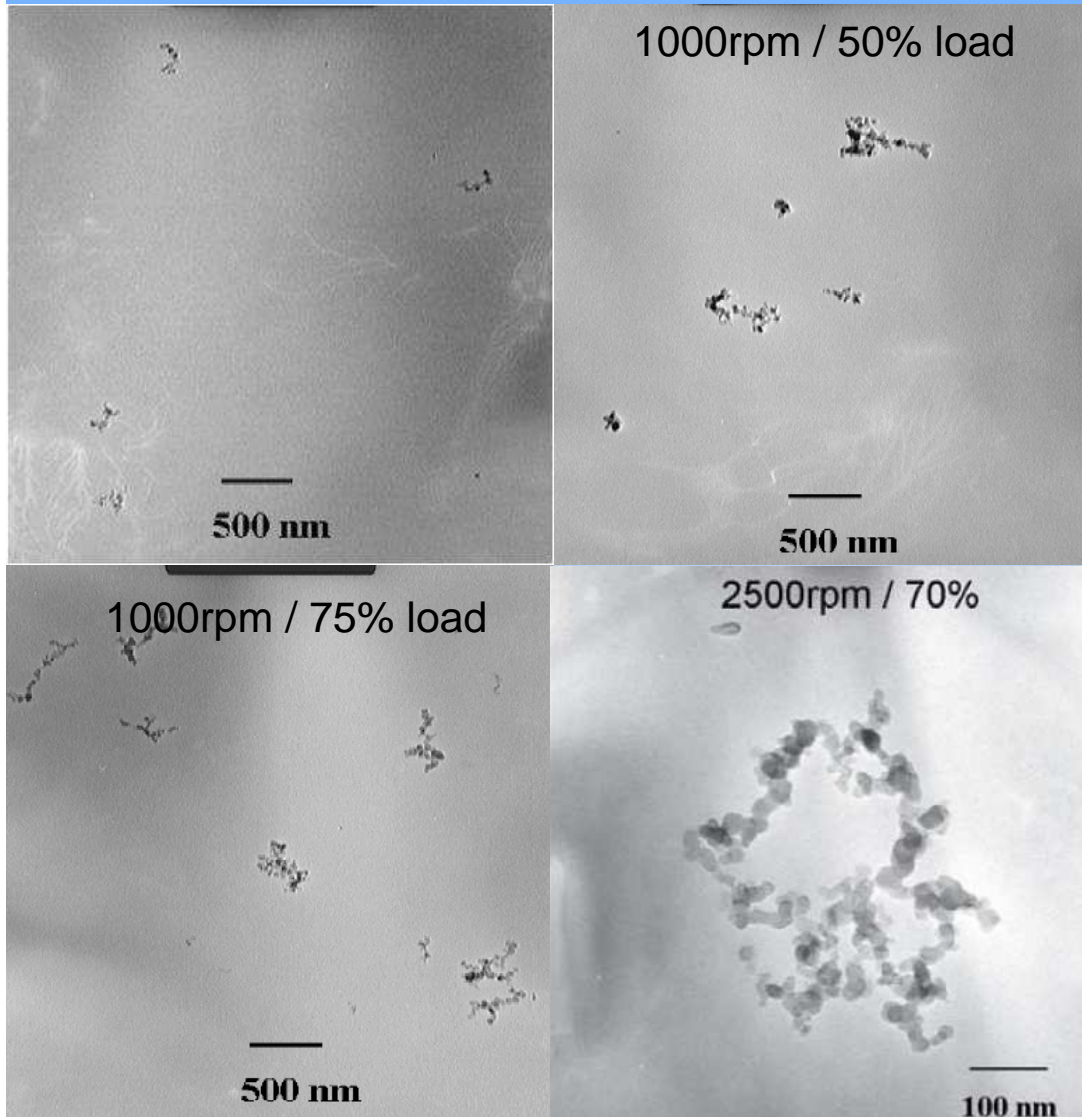
- Background
 - introduction
 - conventional laser-induced incandescence (LII) method
- Auto-compensating laser-induced incandescence (AC-LII) method
 - innovations
 - theory
 - experimental
- Applications
 - engine dyno measurements
 - chassis dyno measurements
 - on-road measurements
 - gas turbine measurements



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TEM images of nanoparticles sampled from a Diesel exhaust

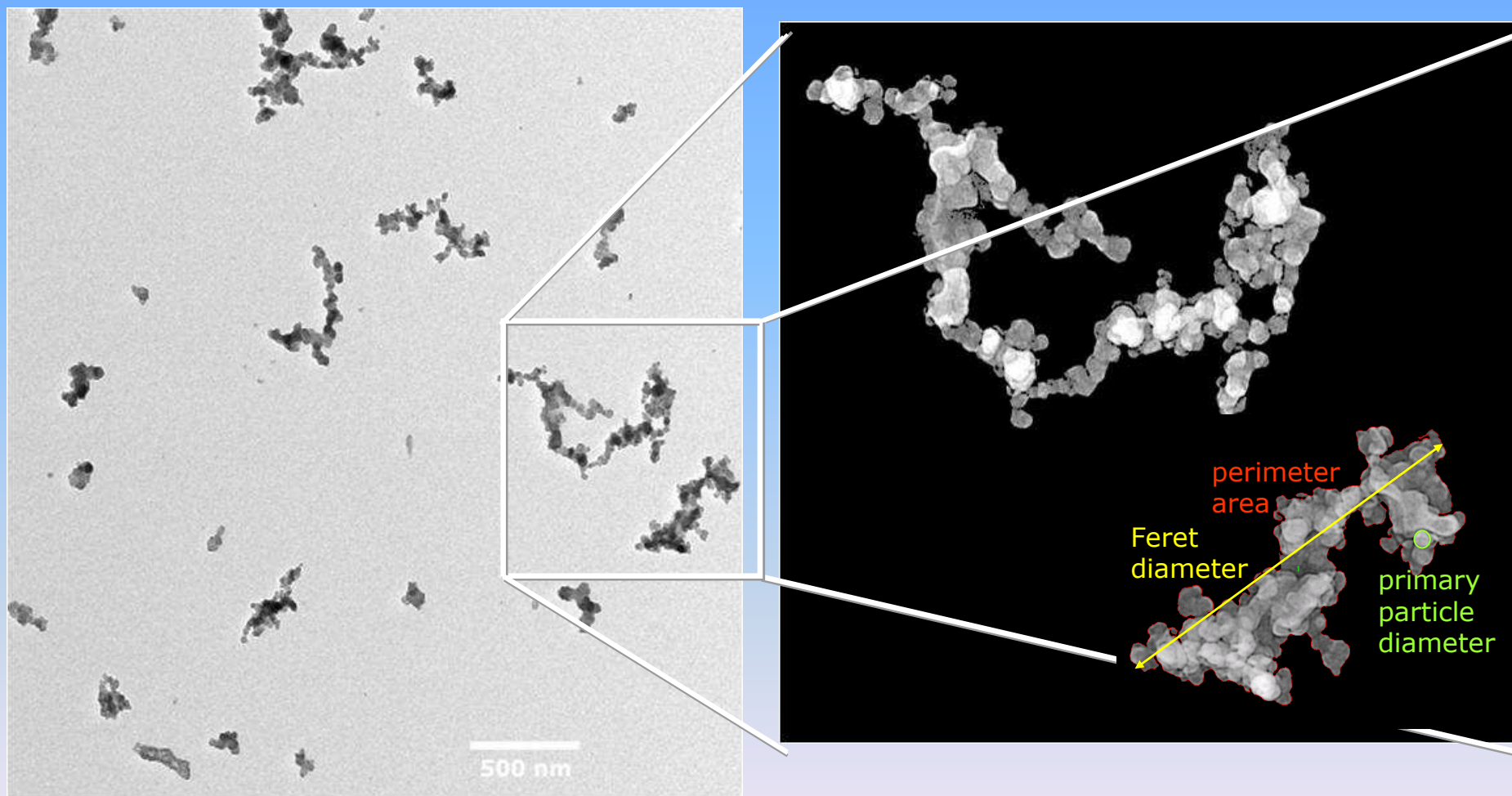


- soot
- carbon black
- black carbon
- elemental carbon
- **refractory carbon**

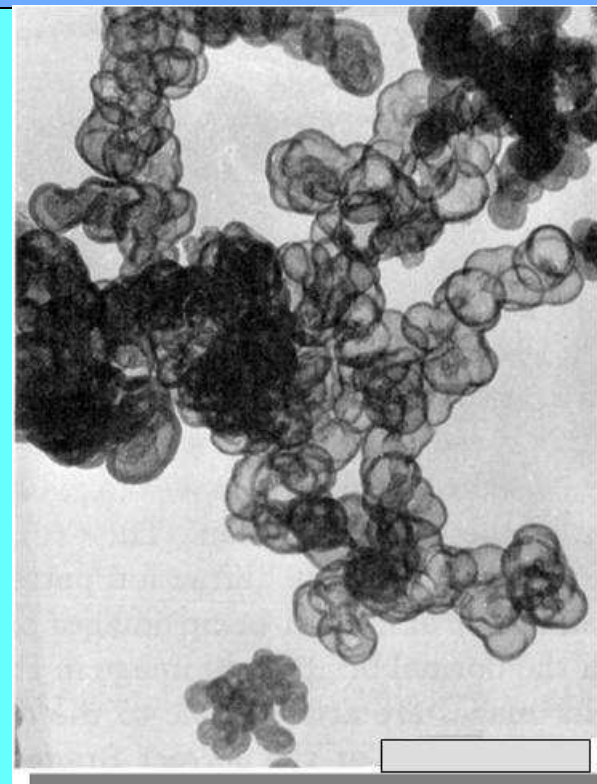
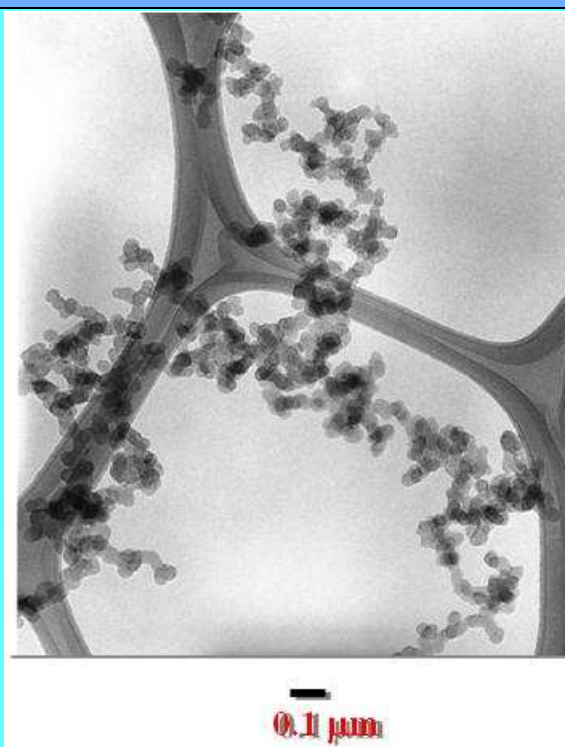
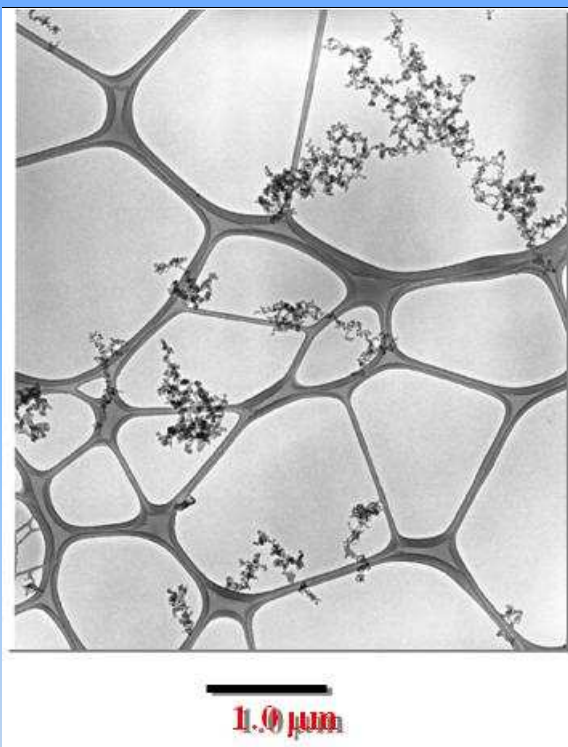
“Life exists in the universe only because the carbon atom possesses certain exceptional properties”

James Jeans

TEM Imaging of Flame Soot



Transmission Electron Microscope (TEM) Images of Soot

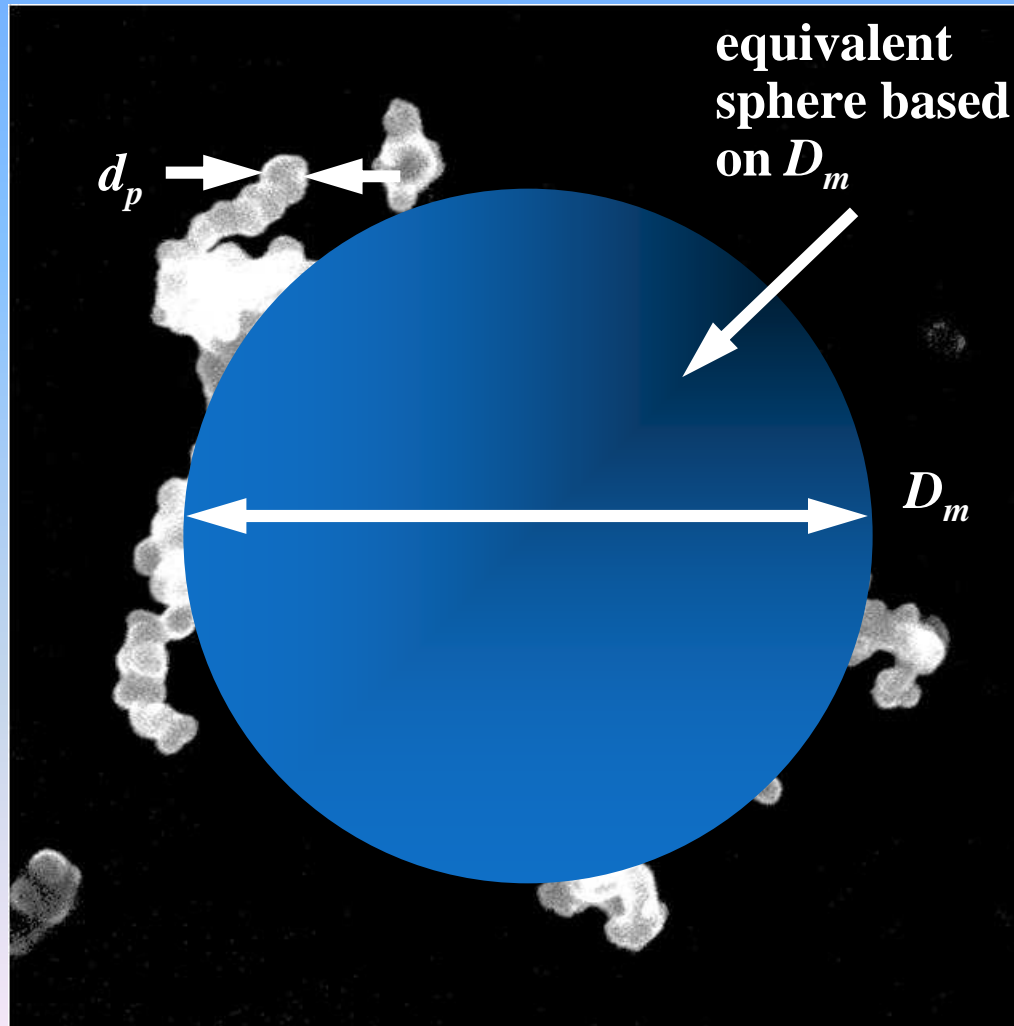


Morphology

- nearly-spherical primary particles 20–50 nm in diameter
- SOF absorbed onto the surface of the primary particles
- Primary particles cluster into chain-like aggregates

SEM Image of Flame Soot

Others assume an “equivalent sphere diameter”, **what's the density?**



What Does LII Do?

- Quantitative measurement for dry soot:
 - concentration (0.5 ppt – 10 ppm volume; $1\mu\text{g}/\text{m}^3$ – $20\text{g}/\text{m}^3$ mass)
 - active surface area (50 – 200 m^2/g)
 - primary particle diameter (typically 5-50 nm)
 - number density of primary particles
- Measurement features:
 - very high precision and repeatability
 - transient concentration
 - nonintrusive (dilution unnecessary)
 - wide range of applicability
 - potential standardized method
 - measures soot
 - uninfluenced by the presence of other species



Technology Licensed from NRC, Canada

NRC Canada/ Artium LII Innovations

- Absolute intensity (patented)
 - spectral radiance calibration
- Real-time two-color pyrometry (patented)
 - particle temperature
- Laser beam profile (patented)
 - uniform heating
- Low laser fluence (patented)
 - no sublimation

Science Behind LII

IVG INSTITUT FÜR VERBRENNUNG UND GASDYNAMIK

UNIVERSITÄT DUISBURG ESSEN

International Bunsen Discussion Meeting and Workshop on
**Laser-induced incandescence:
Quantitative interpretation, modelling, application**
September 25-28, 2005

Universität Duisburg-Essen, Germany

Conference (Monday, Sept. 26)
Workshop (Tuesday and Wednesday, Sept. 27-28)
Location: Haus der Unternehmer, Duisburg

Christof Schulz (IVG, Universität Duisburg-Essen)
Greg Smallwood (NRC Canada, Ottawa)
Bas Bougie (Radboud University Nijmegen)
Coralie Schoemaeker (Université des Sciences et Technologies de Lille)



www.uni-duisburg.de/ivg/vg/lii-workshop
office@ivg.uni-duisburg.de fax: +49 203 379 3087

Co-organized with:




2005

International Meeting and Workshop on
**Laser-induced incandescence:
Quantitative interpretation, modelling, application**
August 2-4, 2006

University of Karlsruhe, Germany
Institut für Technische Chemie und Polymerchemie

Organizers:

Henning Bockhorn and Rainer Sontz
TCP, Universität Karlsruhe

Klaus-Peter Geigle
DLR, Stuttgart

Christof Schulz
IVG, Universität Duisburg-Essen

Greg Smallwood
NRC, Ottawa

Stefan Will
TT, Universität Bremen

Georgio Zizak
CNR-IPEN, Bologna




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www.uni-karlsruhe.de/ict/lii-workshop

2006




THIRD INTERNATIONAL WORKSHOP AND MEETING ON
**LASER-INDUCED INCANDESCENCE:
QUANTITATIVE INTERPRETATION,
MODELING, APPLICATION**

July 30 to August 1, 2008, Ottawa, Canada

National Research Council of Canada
Institute for Chemical Process and Environmental Technology

Find out more | www.liisience.org

E-mail | LIiWorkshop.icpet@nrc-cnrc.gc.ca

Contact | Greg Smallwood: +1-613-993-1391
Kevin Thomson: +1-613-991-0868
Fax: +1-613-957-7869

Canada National Research Council Canada Conseil national de recherches Canada

Canada

2008

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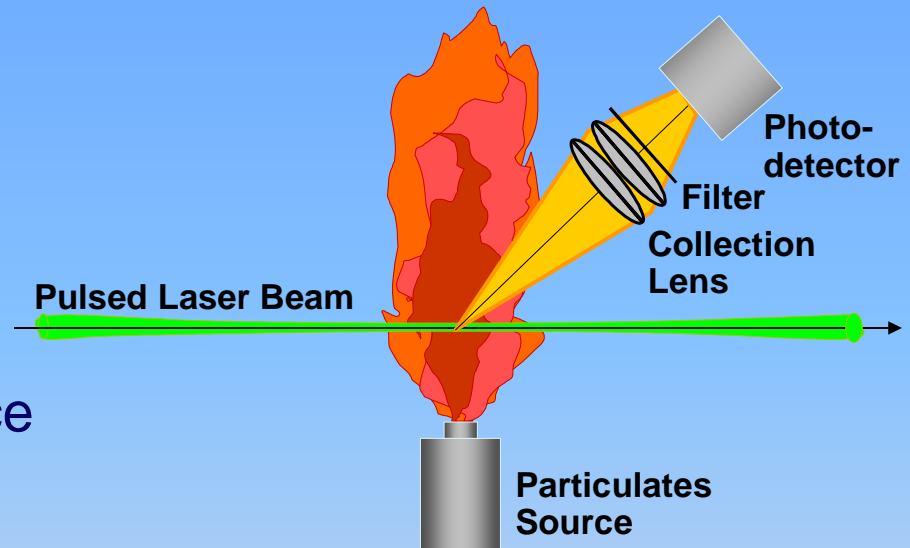
LII Concepts

- **LII experiment:**

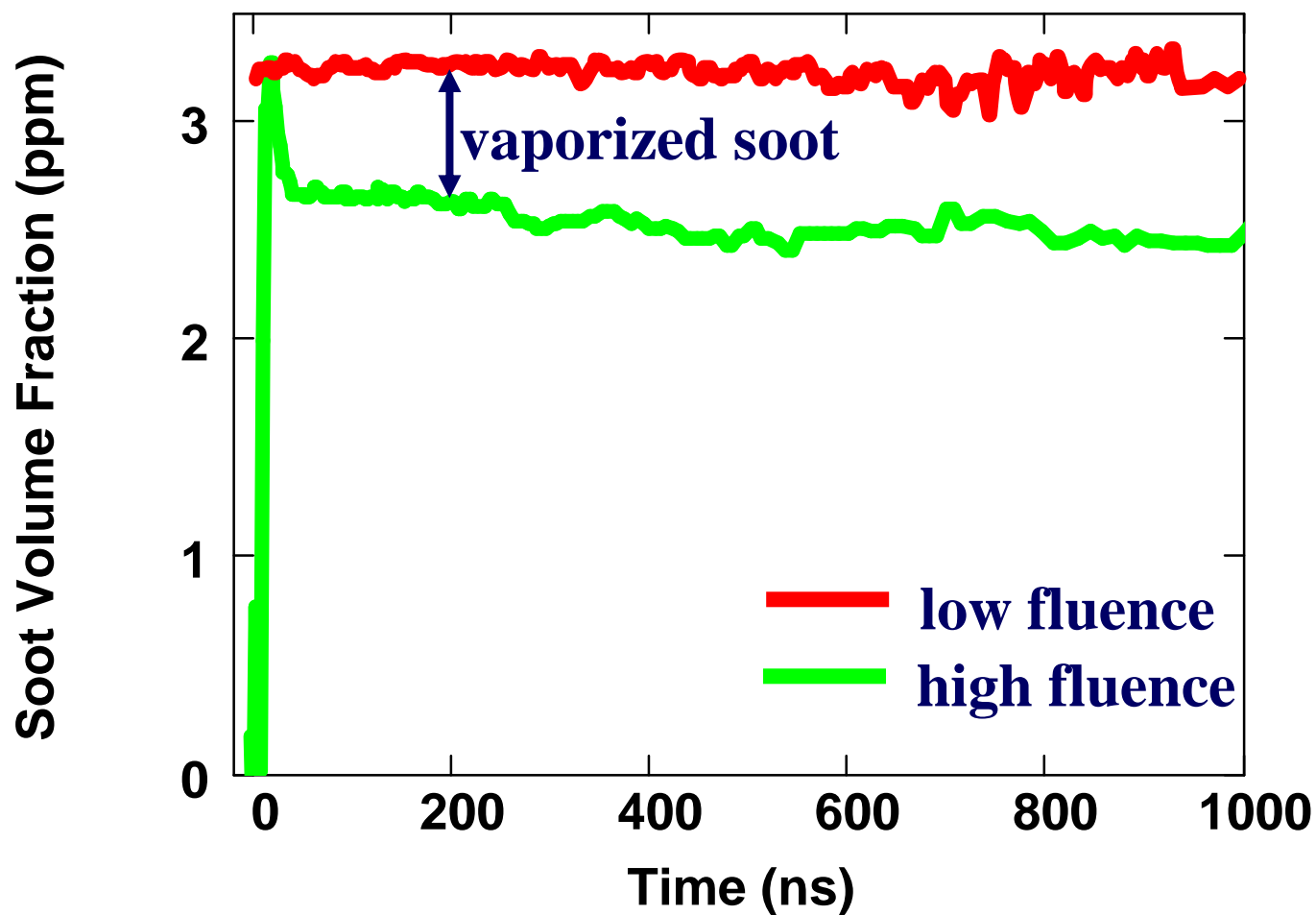
- pulsed laser beam
- rapid heating of soot to evaporation temperature
- soot radiates incandescence as it cools to ambient temperature
- incandescence signal is collected to determine soot concentration, surface area, and primary particle diameter

- **LII theory**

- a state-of-the-art numerical model of nanoscale (time and space) heat transfer to and from the particles



Soot Volume Fraction – Fluence Effects



Auto-Compensating LII (AC-LII)

- **Two-color pyrometry** coupled with LII to determine the time-resolved particle temperature
 - permits use of low-fluence
 - particles are kept below the sublimation temperature
- This new technique ***automatically compensates*** for any changes in the experimental conditions
 - fluctuations in local ambient temperature
 - variation in laser fluence
 - laser beam attenuation by the particulate matter
 - desorption of condensed volatile material

Soot Particle Heat Transfer Equation

$$\underbrace{\frac{\pi D^3}{6} \rho_s c_s \frac{dT}{dt}}_{\text{I}} = \underbrace{C_a q}_{\text{II}} - \underbrace{\frac{2 k_a (T - T_0) \pi D^2}{(D + G \lambda_{MFP})}}_{\text{III}} + \underbrace{\frac{H_v}{M_v} \frac{dM}{dt}}_{\text{IV}} + \underbrace{q_{rad}}_{\text{V}}$$

- I change in internal energy
- II laser heating
- III heat transfer to surrounding gas
- IV soot sublimation
- V radiative heat loss

Particulate Concentration

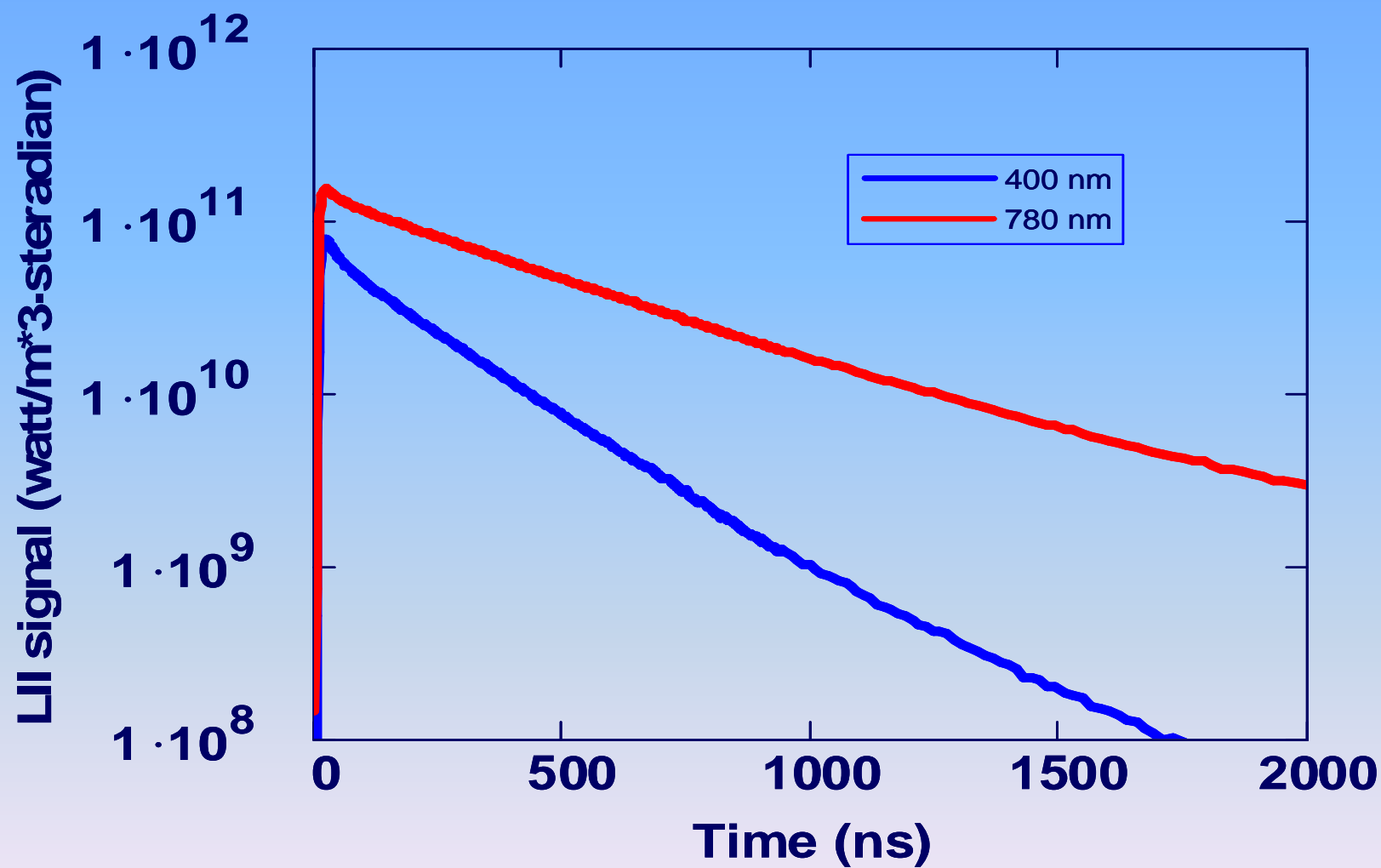
- Determine calibration factor

$$\eta(\lambda) = \frac{V_{CAL}(\lambda)}{R_S(\lambda, T)}$$

- Measure incandescence, $P_p(\lambda)$, at two wavelengths and solve for temperature, T

$$\frac{P_p(\lambda_1)}{P_p(\lambda_2)} = \frac{\lambda_2^6}{\lambda_1^6} \frac{\left(e^{\frac{hc}{k\lambda_2 T}} - 1 \right)}{\left(e^{\frac{hc}{k\lambda_1 T}} - 1 \right)} \frac{E(m_{\lambda_1})}{E(m_{\lambda_2})}$$

Absolute LII Signals



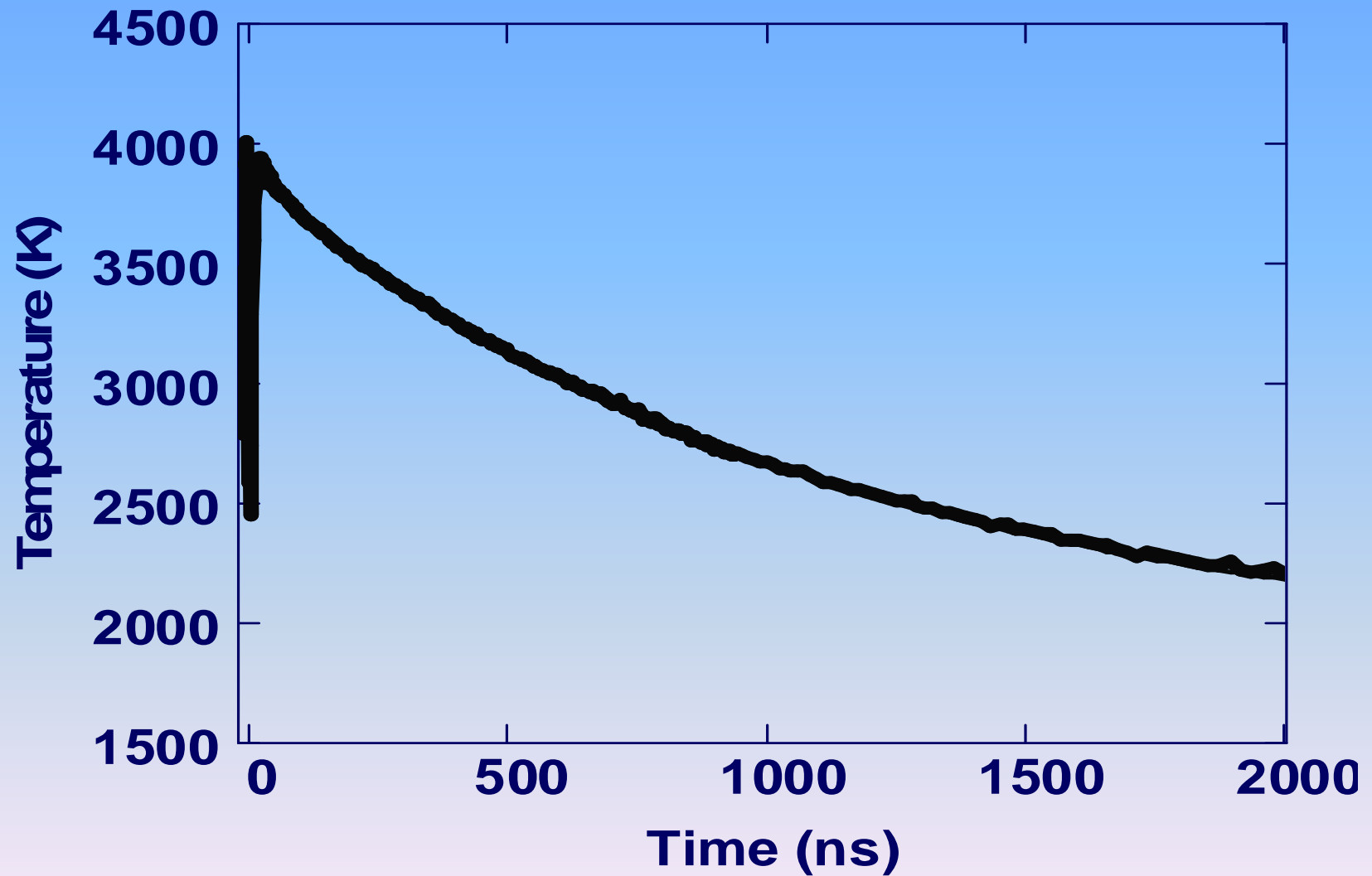
Two-Color Pyrometry

- relative signal at two wavelengths:

$$\frac{V_{EXP}(\lambda_1)}{V_{EXP}(\lambda_2)} = \frac{\eta(\lambda_1)}{\eta(\lambda_2)} \cdot \frac{\lambda_2^6}{\lambda_1^6} \cdot \frac{\left(e^{\frac{hc}{k\lambda_2 T}} - 1\right) E(m_{\lambda_1})}{\left(e^{\frac{hc}{k\lambda_1 T}} - 1\right) E(m_{\lambda_2})}$$

- where:
 - V_{EXP} is the LII measured signal (volts)
 - λ_1 and λ_2 are the detection wavelengths for each channel
 - η is the calibration factor (relating measured volts to the source radiance)
 - h , c , and k are the Planck constant, velocity of light, and Boltzmann constant, respectively
 - T is the temperature (K)
 - $E(m)$ is the absorption function, an optical property of soot
- the equation is solved to determine temperature

Real-Time Temperature



Particulate Concentration

- The particle (soot) volume fraction is known to be

$$f_v = n_p \cdot \frac{\pi d_p^3}{6}$$

- Combining the above equation with the calibration factor and the particle temperature leads to

Soot Volume Fraction

- soot volume fraction:

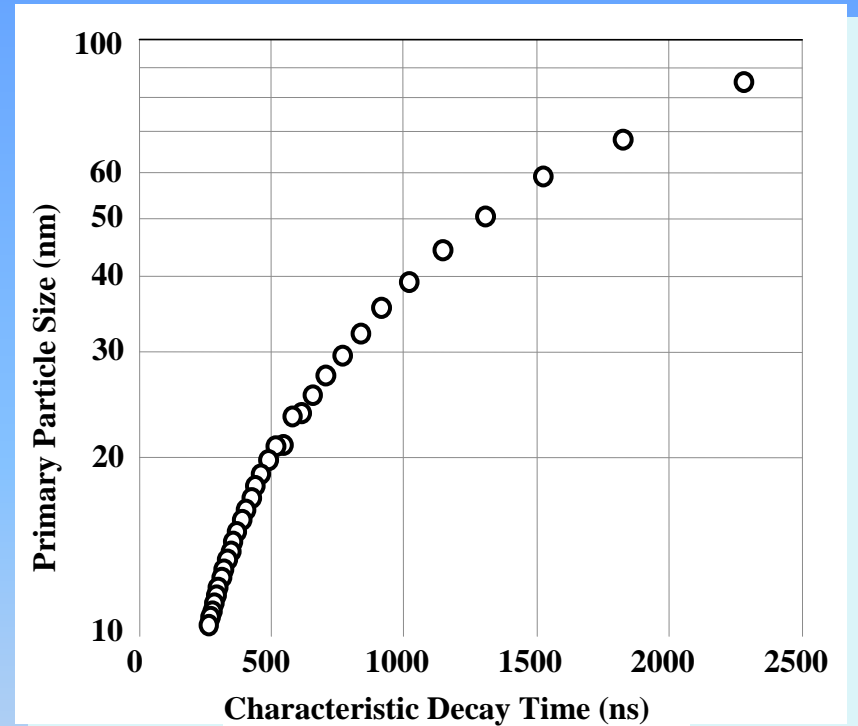
$$f_v = \frac{V_{EXP}(\lambda)}{\eta(\lambda) w_b} \frac{\lambda^6 \left(e^{\frac{hc}{k\lambda T}} - 1 \right)}{12 \pi c^2 h E(m_\lambda)}$$

- where:
 - w_b is the laser sheet width, which determines the depth of the measurement volume
 - the other parameters are the same as described previously
- the area of the measurement volume is the same as the area observed with the calibration lamp, and all the optics and electronics (filters, lenses, photomultipliers, amplifiers, etc.) are the same for the calibration and the LII measurement
- note that the soot volume fraction is inversely proportional to $E(m)$, the soot absorption function

Primary Particle Size

- The temperature differential between the particle surface and the ambient gas decays steadily in an exponential manner

$$T - T_g = A \cdot e^{-t/\tau}$$



- The primary particle diameter may be inferred (*McCoy and Cha, 1974*)

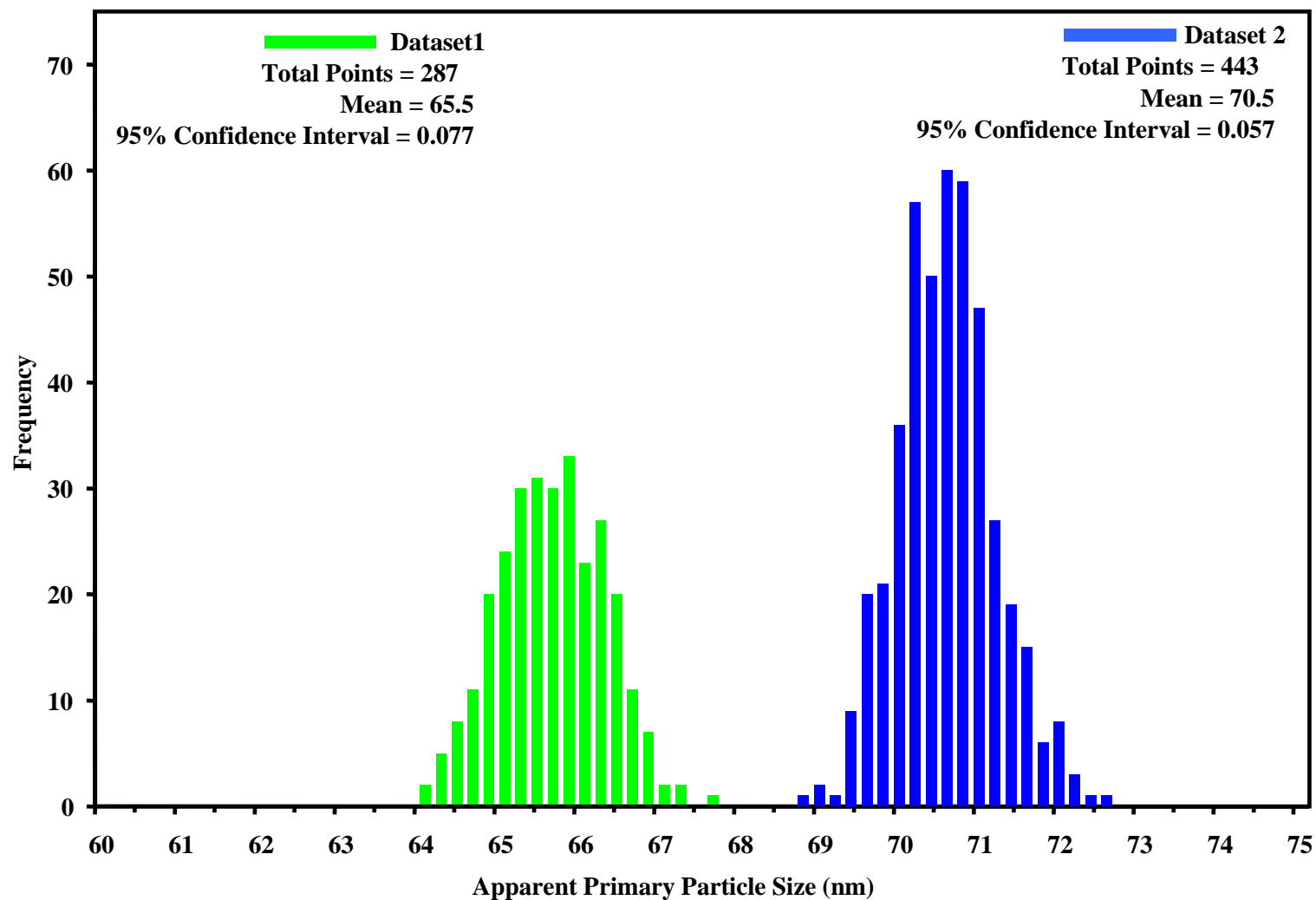
$$d_p = \frac{12k_g \alpha}{G \lambda_{MFP} c_p \rho_p \tau}$$

Characteristic
decay time



Soot primary Particle Size at Two Combustion Conditions

Carbon Black Production



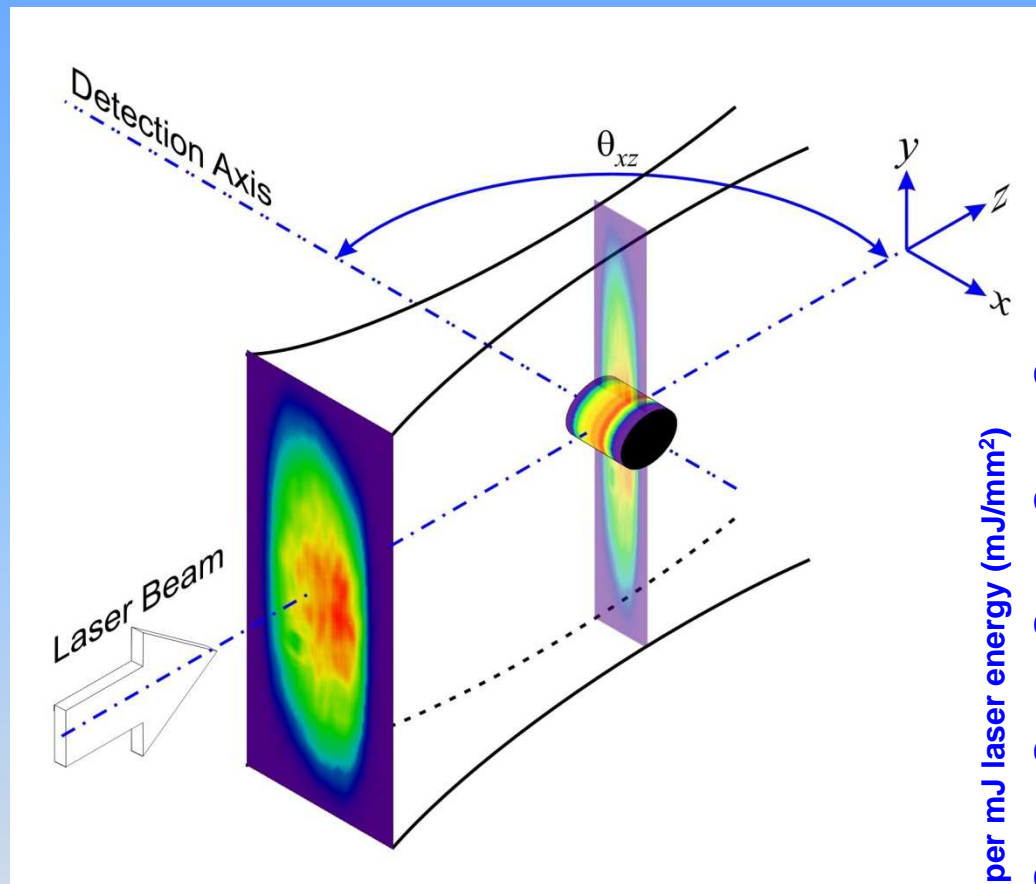
Primary Particle Size: Discussion

- the number of primary particles is also determined
- primary particle size can also be used to determine active surface area
- aggregate size is of greater interest from the health, environment, and regulation perspectives
- knowledge of primary particle size and number provides insight about aggregate morphology

What Do We Need to Know in Advance?

- calibration source
 - spectral radiance
- optics
 - absolute optical filter transmission
 - relative dichroic mirror reflectivity
 - relative interference filter transmission
- electronics
 - relative photodetector sensitivity
 - photodetector gain
 - amplifier gain
- dimensions of probe volume
- laser spatial fluence profile

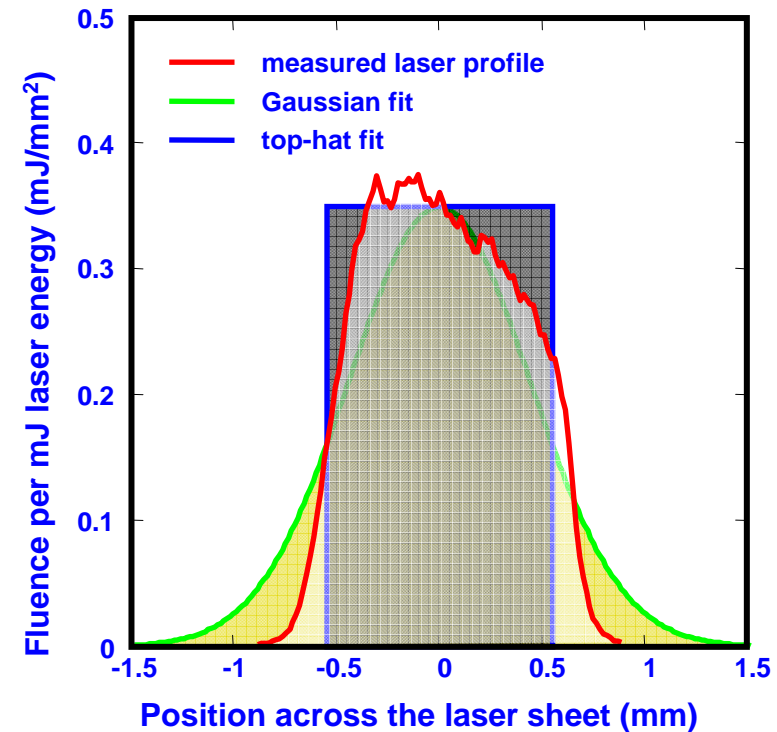
Laser Light Beam Spatial Profile



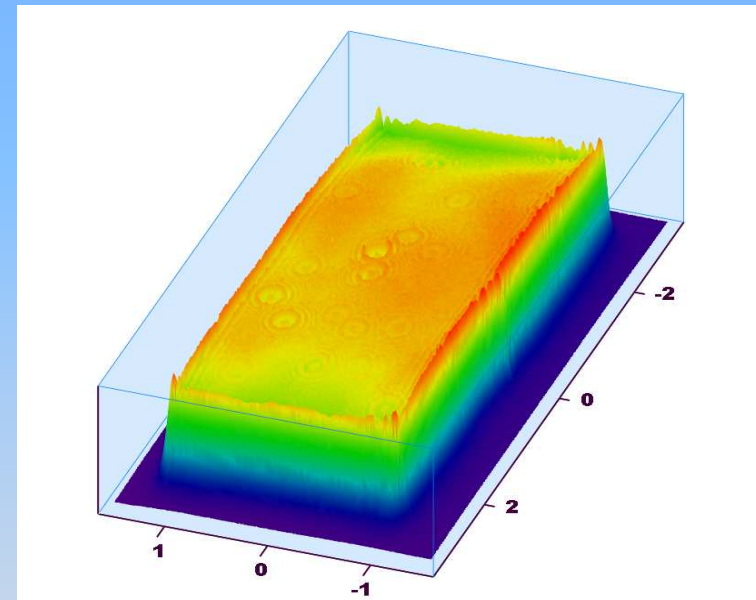
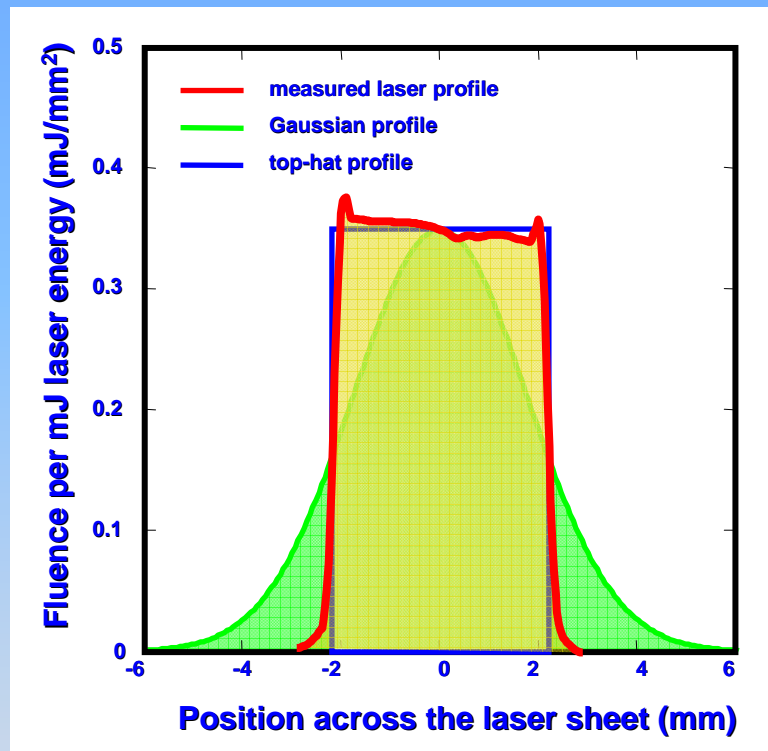
- each fluence level will heat particles to a different temperature
- ideal is a top-hat profile

↑ Gaussian sheet

multimode "tophat" ⇒

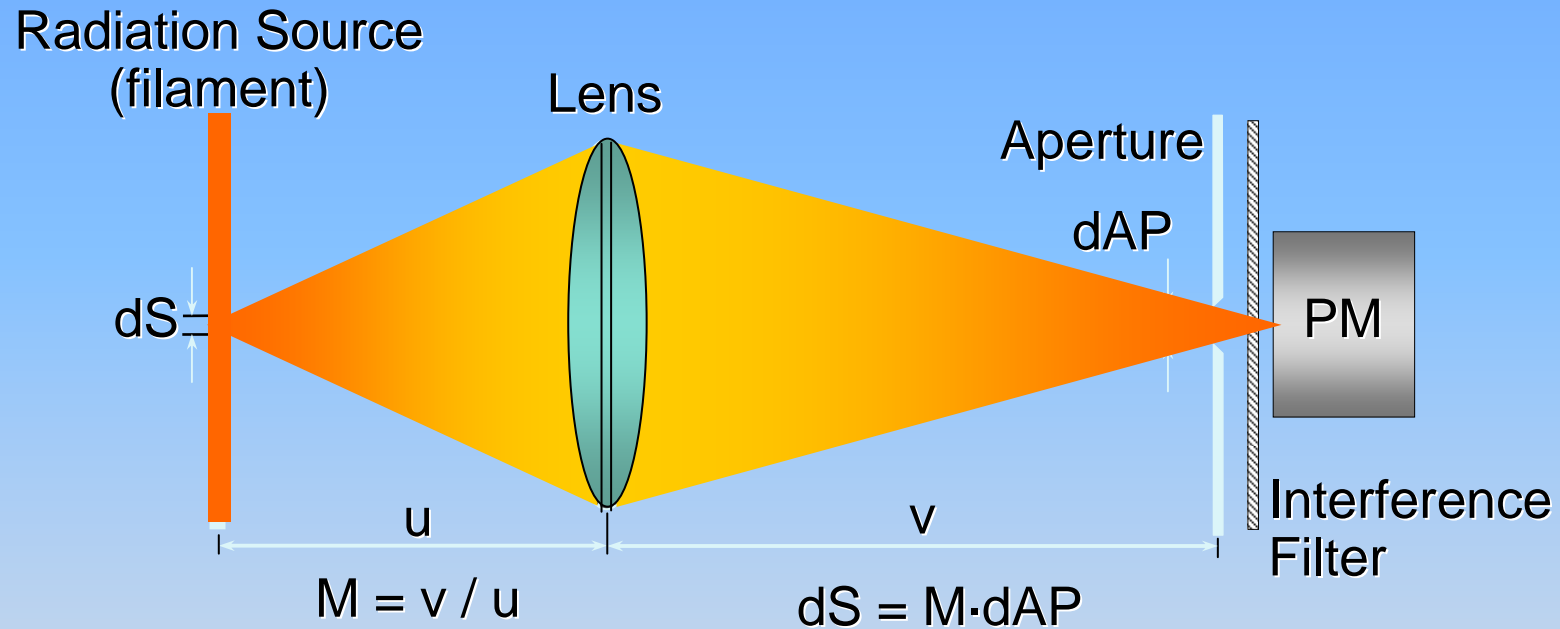


Relay Imaging for Top Hat Profile



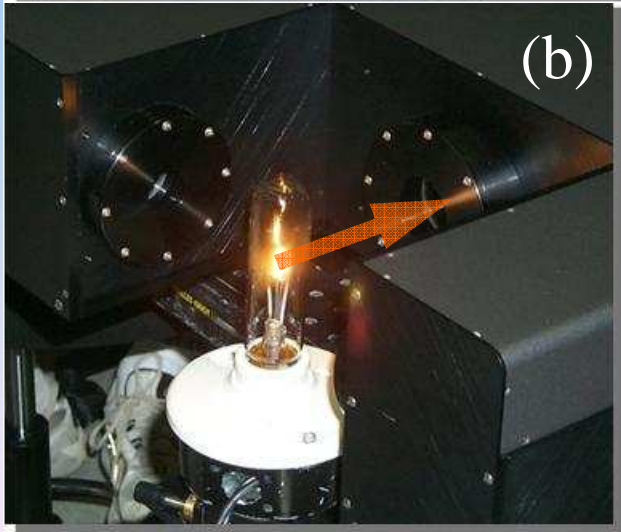
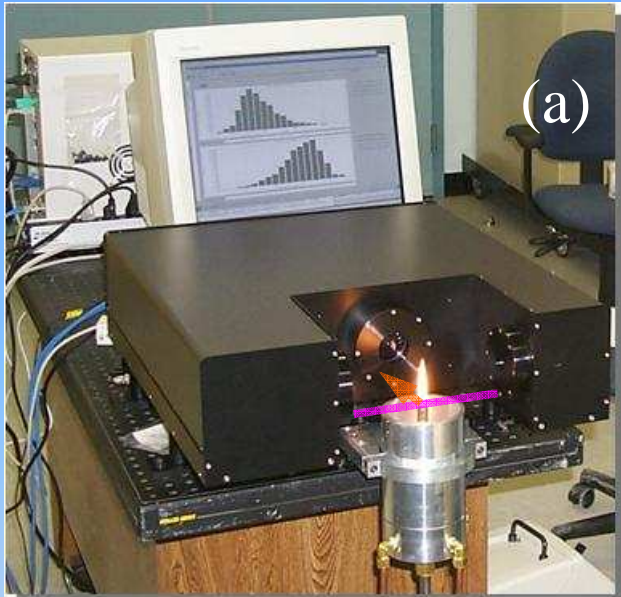
- place rectangular aperture in laser beam
- relay image aperture to probe volume location

Absolute Intensity Calibration



- use two-color pyrometry to determine the filament temperature
- use known filament radiant power incident on the aperture to calibrate the detection system (NIST-traceable spectral radiance calibration)

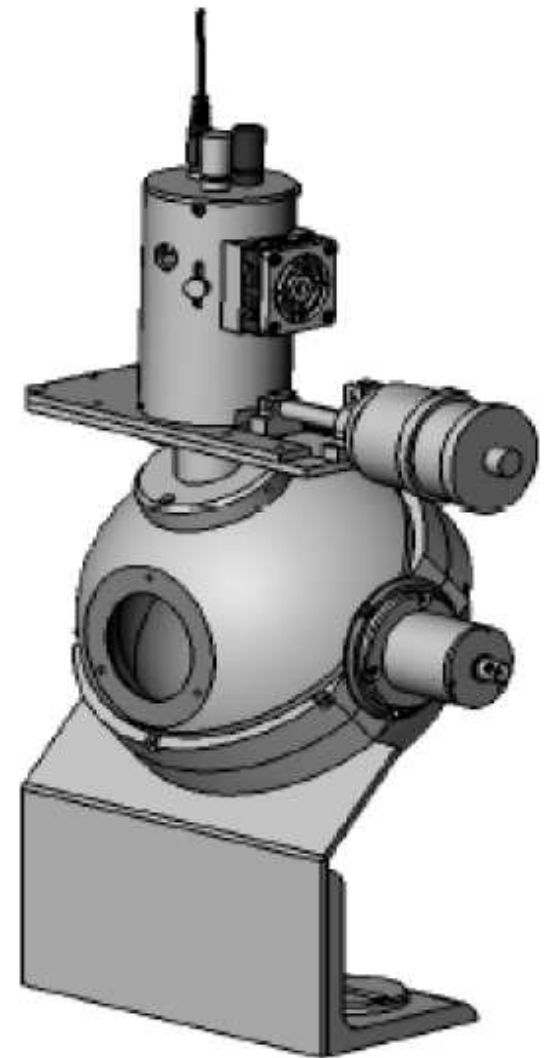
Artium Technologies LII Instrument



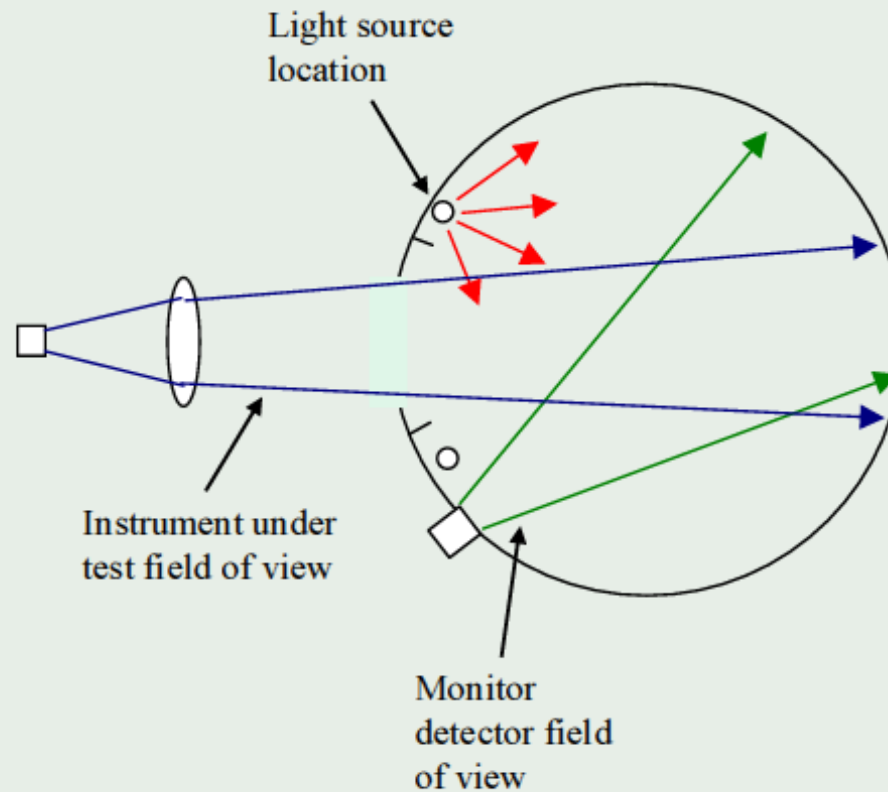
- a) Soot source in measurement volume
(sampling cell removed to aid illustration)
- b) Lamp replacing soot as source of incandescence
- NIST – traceable calibration procedure
 - lamp is a calibrated spectral radiance source, in $\text{Watts/m}^3\text{-steradian}$
 - tungsten strip filament lamp is used
 - photomultiplier signal is recorded for a number of calibrated filament temperatures to ensure accurate calibration
 - a single calibration factor, η , is determined for each wavelength channel (400 nm and 780 nm)
 - electronic gain of photomultiplier (PM) is independently calibrated for different PM bias voltages

Luminance / Radiance Standards

- Traceable Luminance & Radiance Standards
- <1" to >24" Port Sizes
- Low-Light Level Calibration (Night Vision)
- CCT/Spectral Monitoring
- Variable Output Levels
- Custom Solution Designs



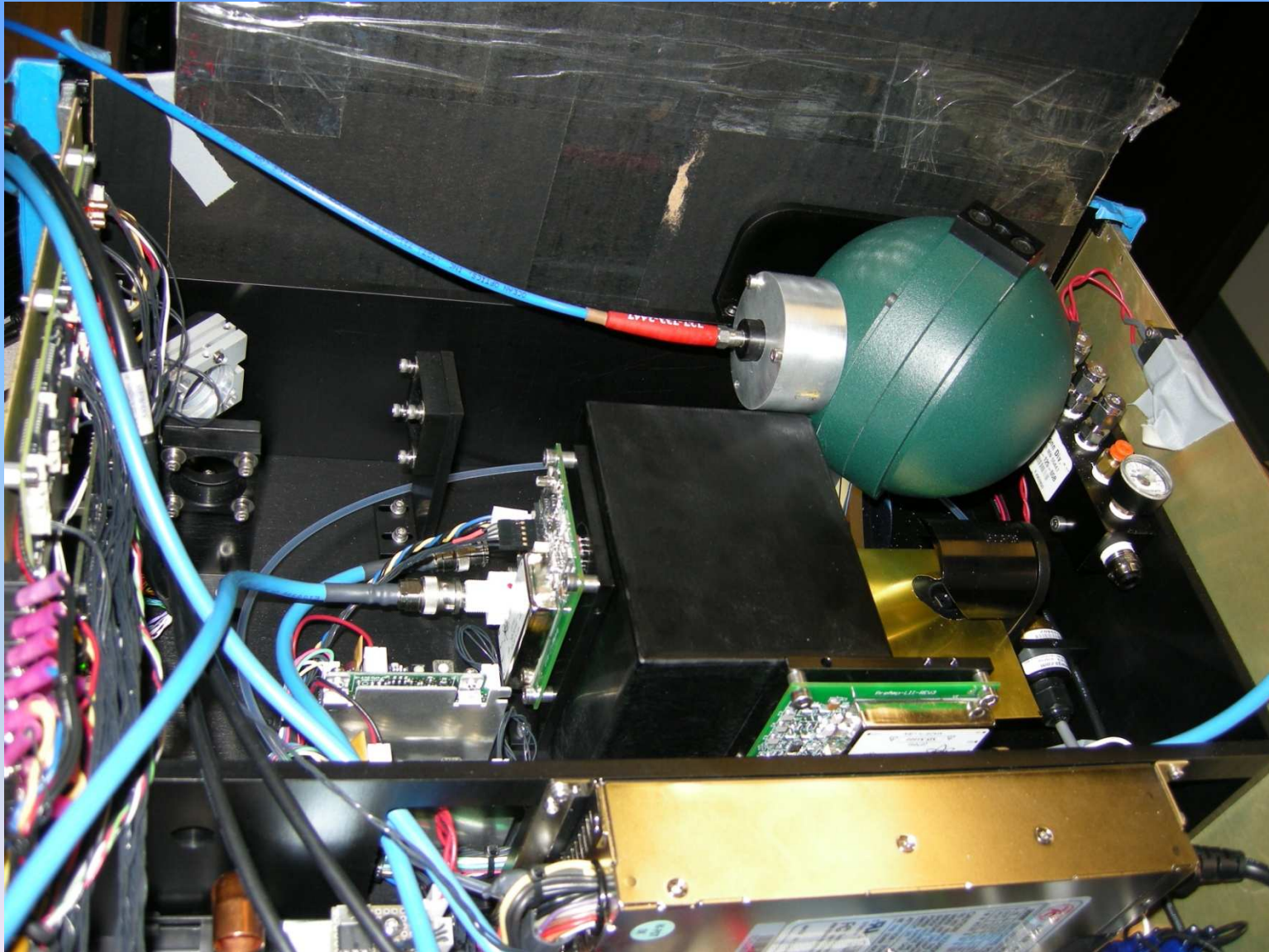
Radiance Standard Anatomy



Sphere Radiance

$$= \frac{\phi_i}{\pi A_s} * \frac{\rho_0}{1 - \bar{\rho}}$$

Calibration with Integrating Sphere/Spectrometer

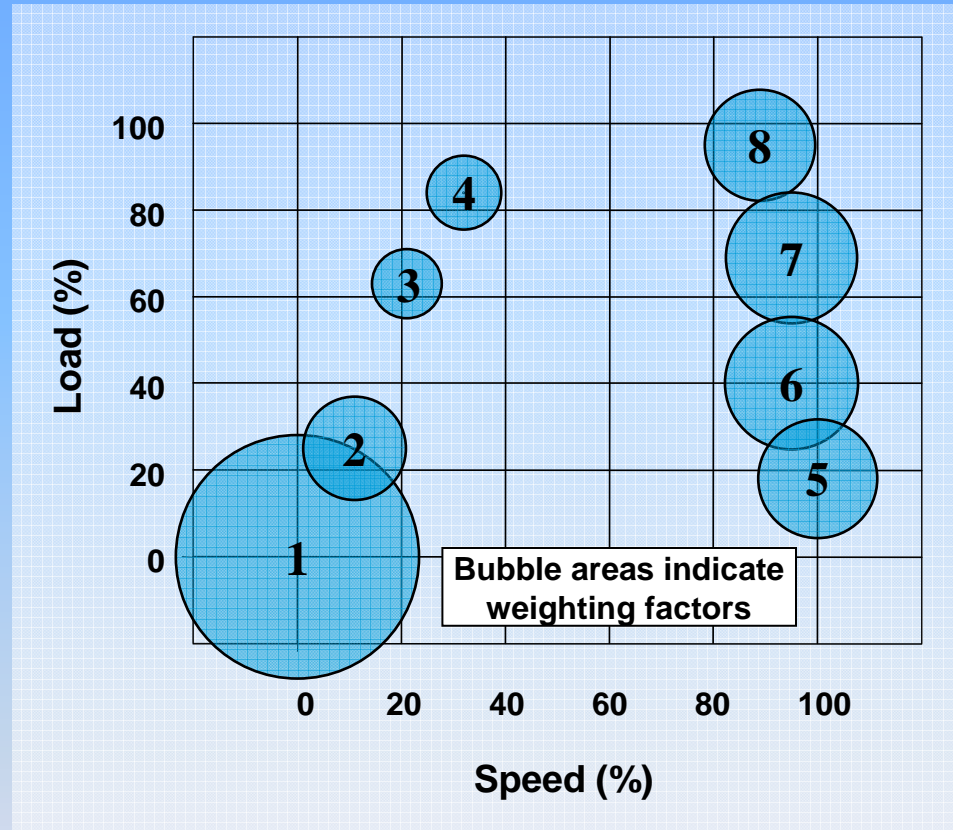
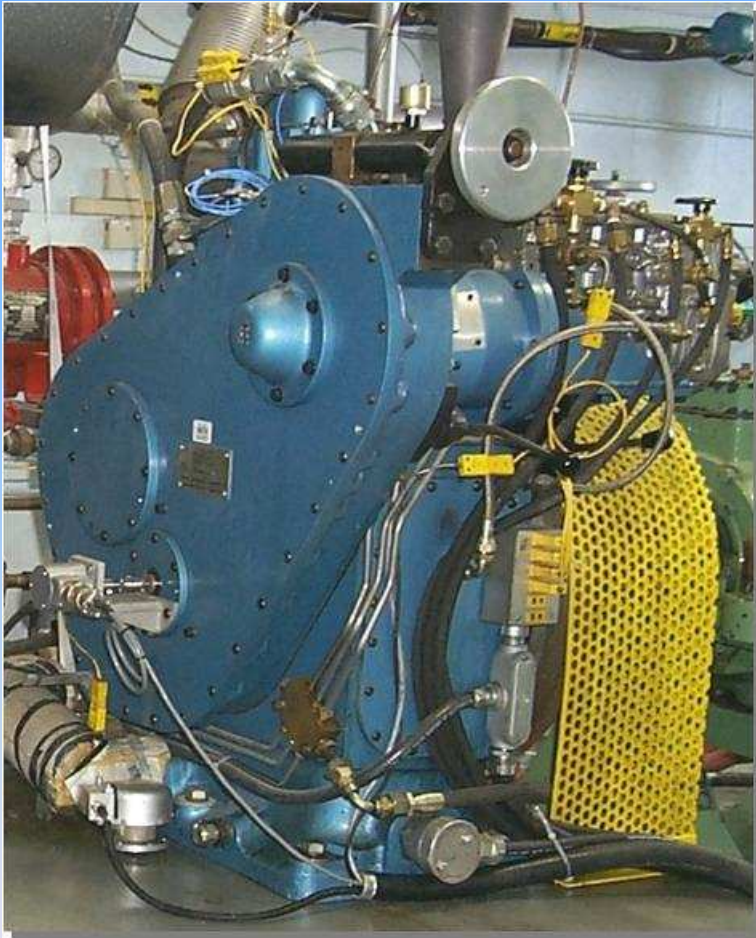


LII TESTING AND VALIDATION

Testing Includes:

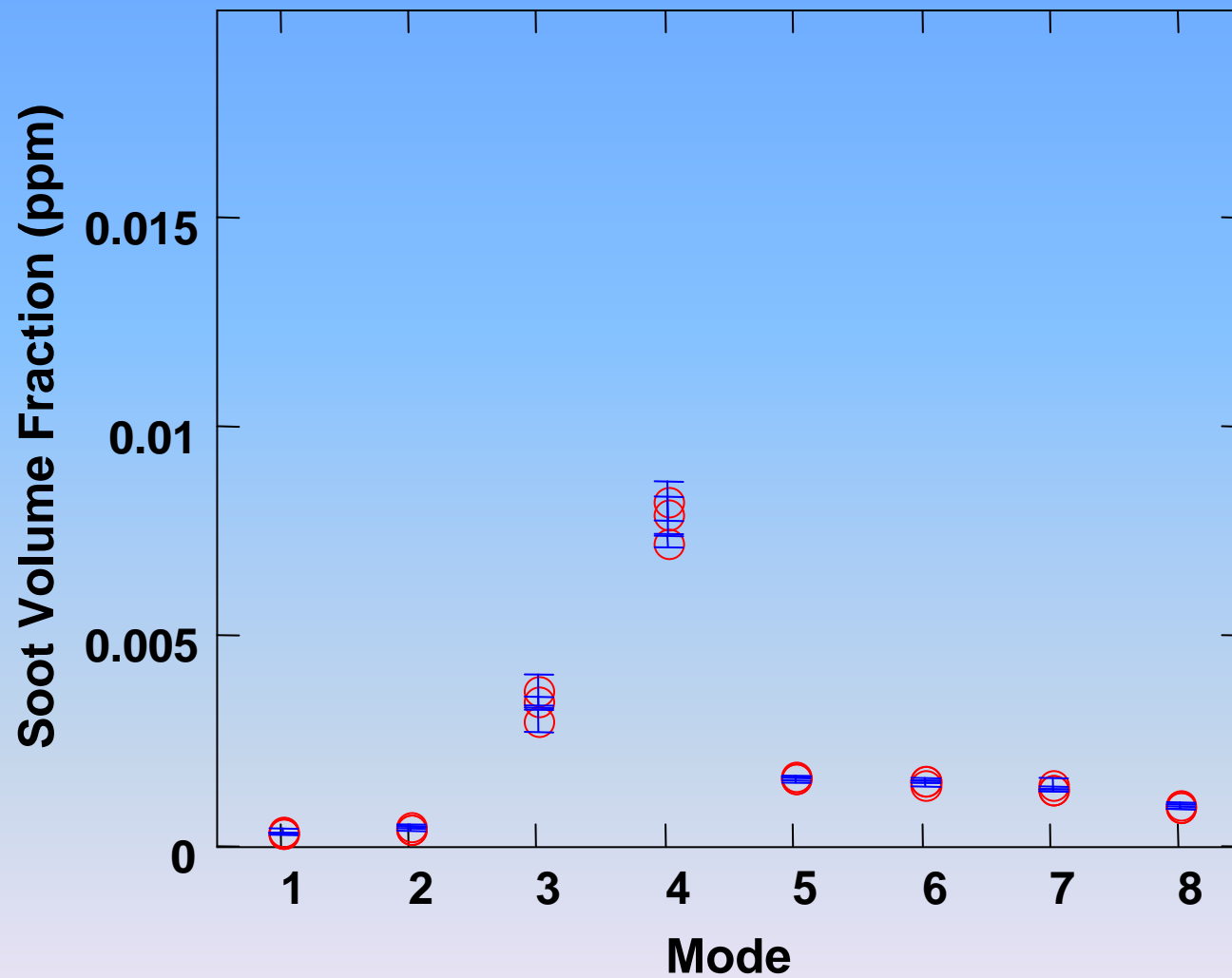
- Laboratory diesel engines
- HD Diesels on dynamometers
- On road testing of HD and LD Diesel emissions
- Turbine engine emissions
- Comparisons to Gravimetric and other optical and filter based methods

Applications – Engine dyno measurements



**Ricardo Heavy Duty Diesel Engine
AVL 8-Mode Steady-State Simulation**

HD Diesel Soot Concentration



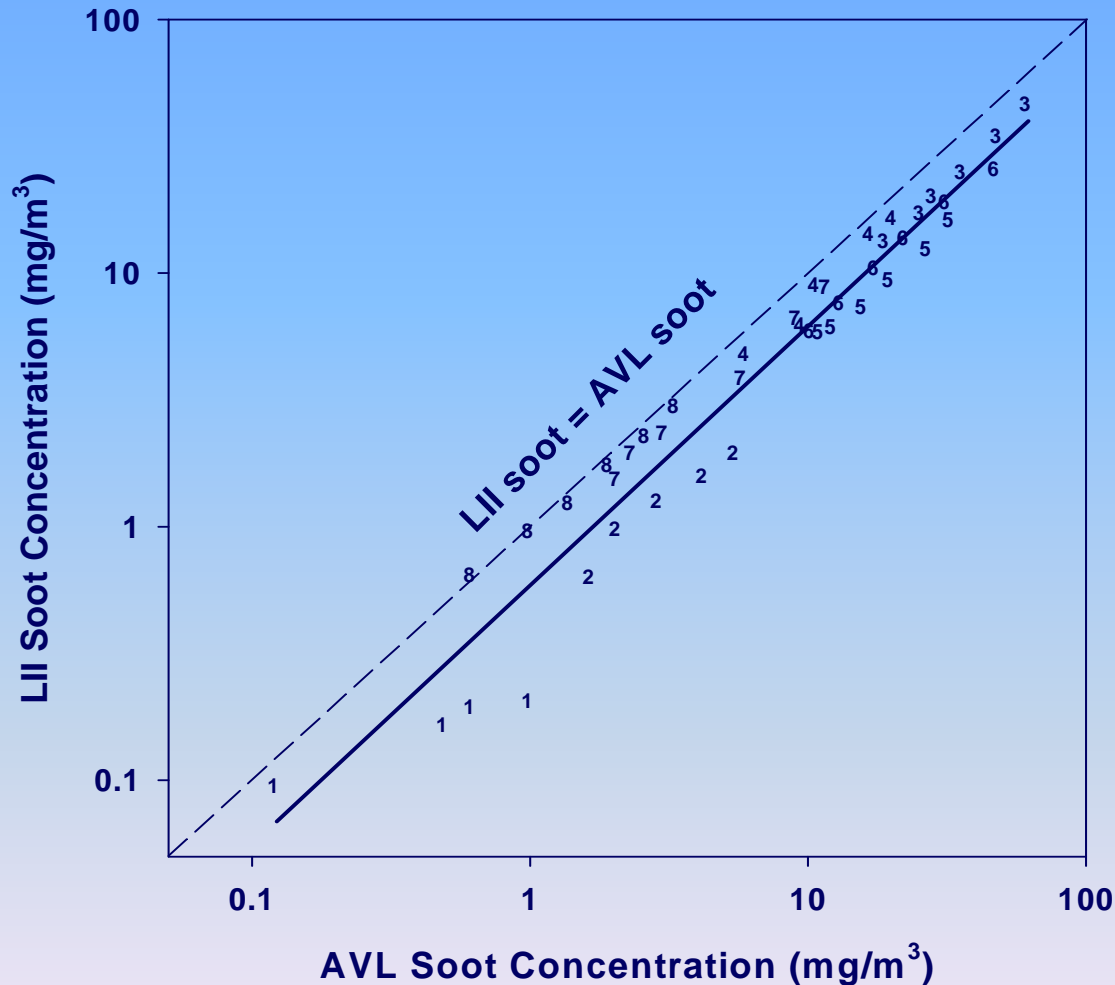
Single Cylinder Heavy-Duty Diesel Engine



Caterpillar 3401E (NRC Prototype 2004)

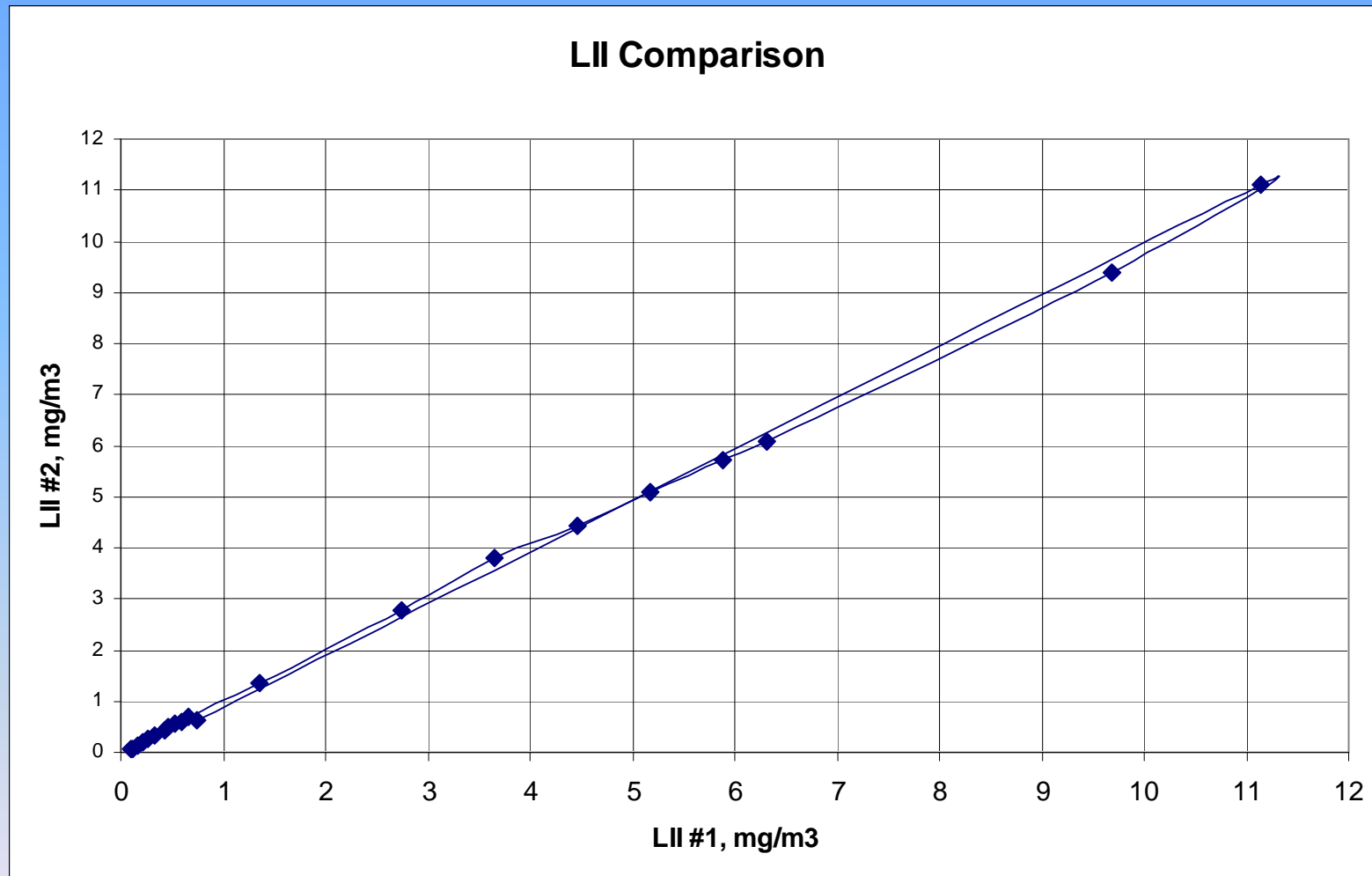
Cylinders	1
Volume	2.44 liters
Comp. Ratio	16.25:1
Peak Power (@1800 rpm)	74.6 kW
Valves	4
Injection	EUI
EGR	Cooled

Diesel PM: Soot Concentration

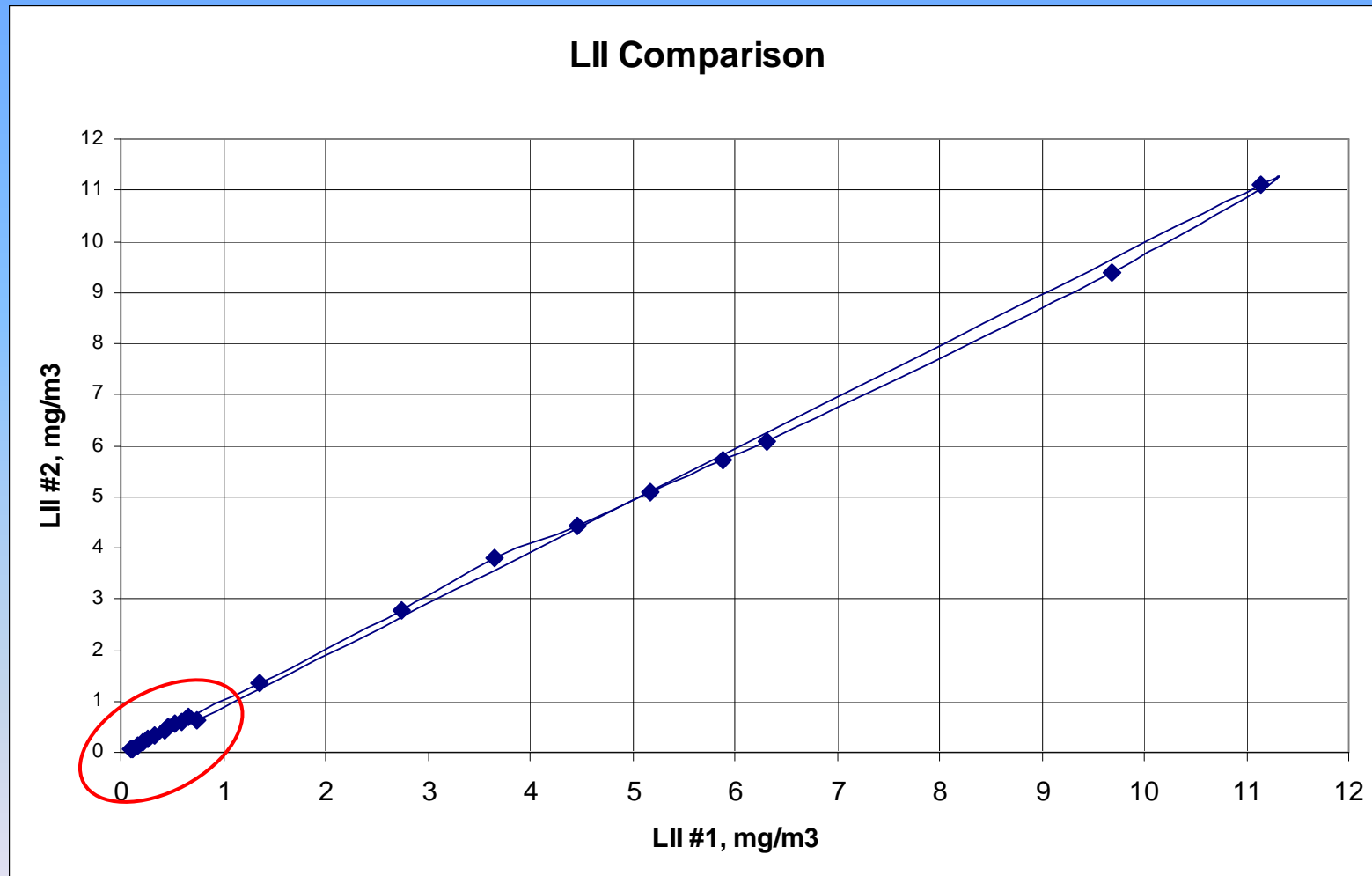


- LII and AVL **Smoke Meter** correlate well over a wide range of engine conditions
- more than two orders of magnitude variation in concentration
- evidence suggests that SOF plays a role, particularly at mode 1

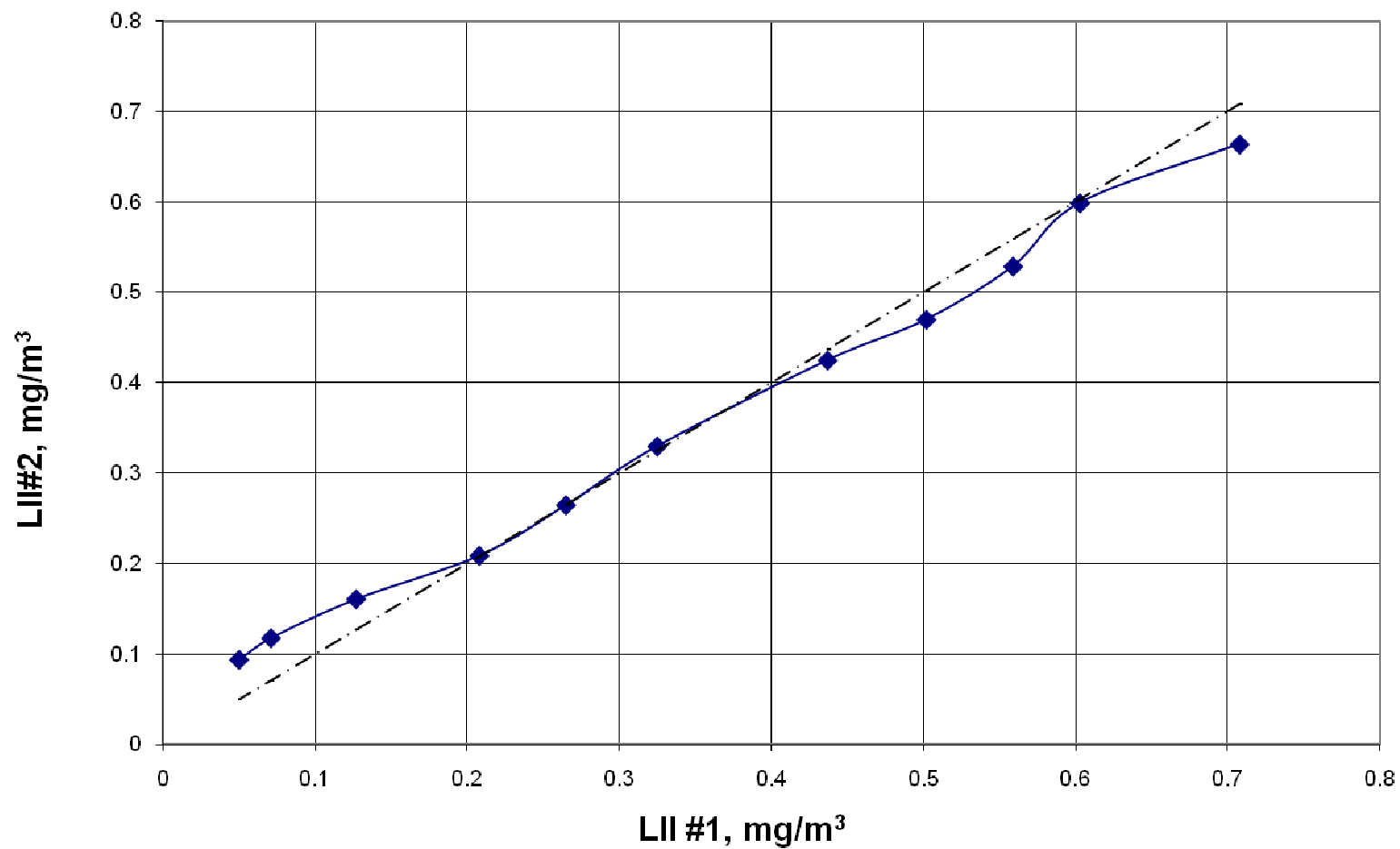
LII-200 Instrument Comparison



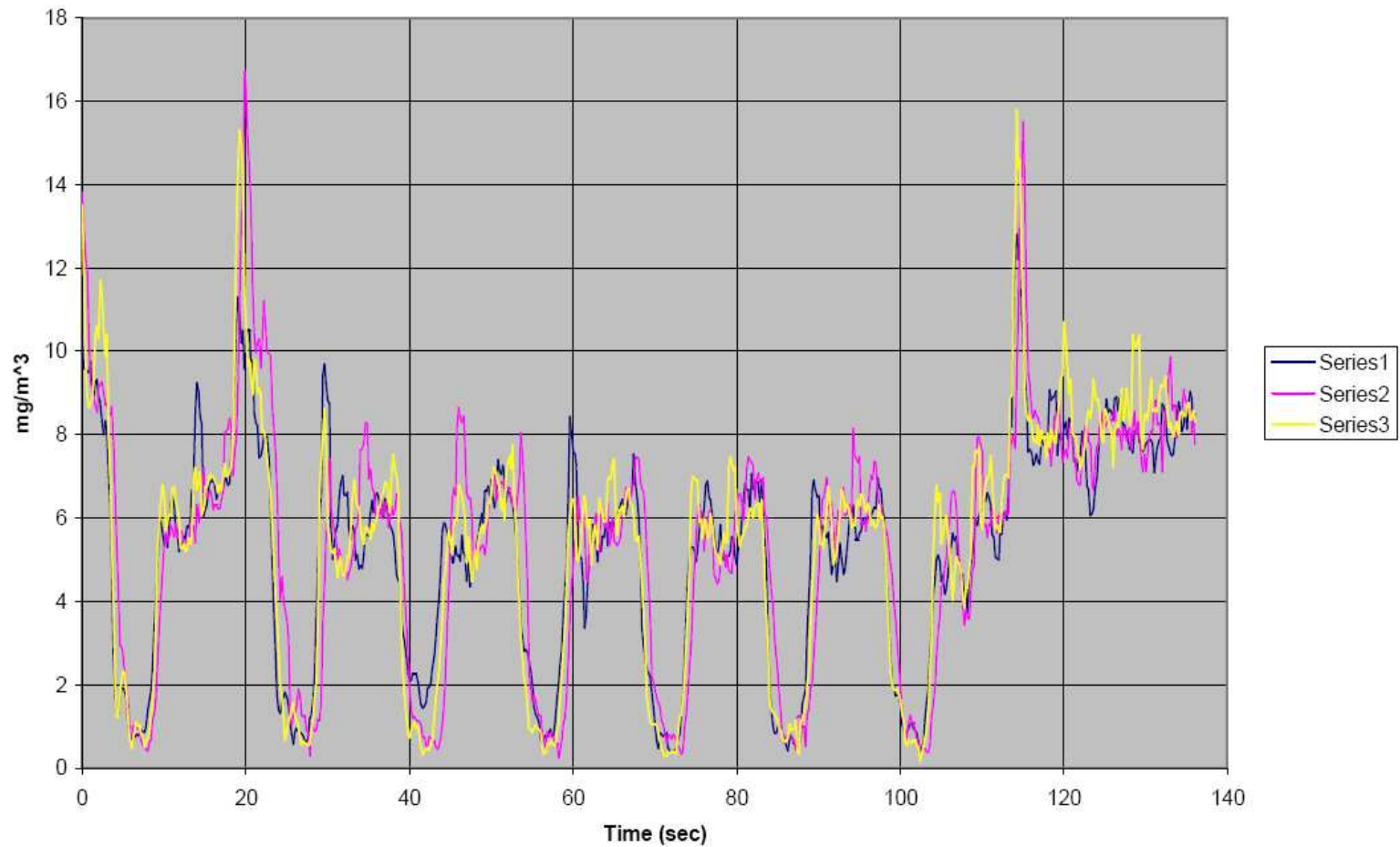
LII-200 Instrument Comparison



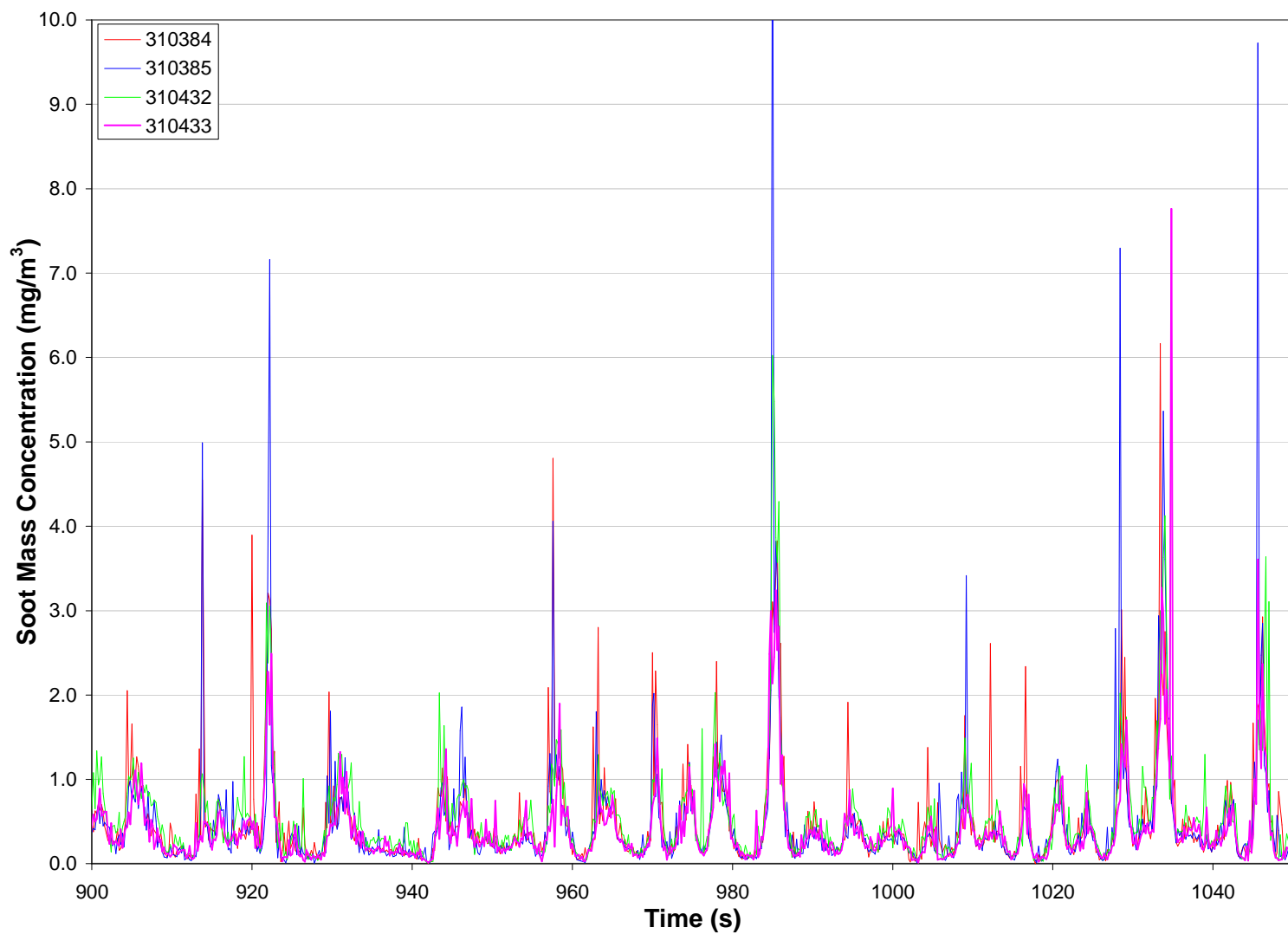
LII-200 Instrument Comparison



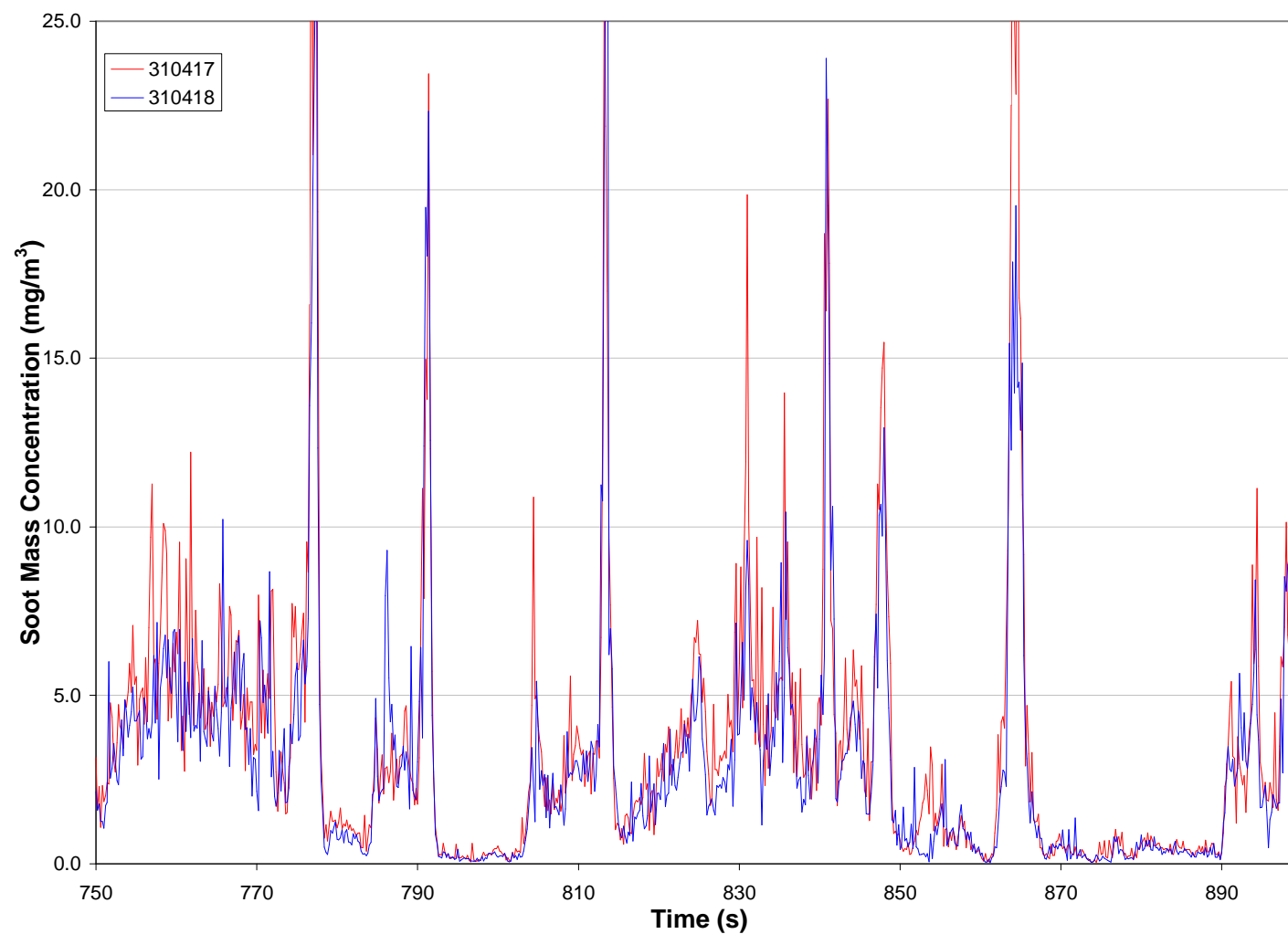
Diesel Cycle Measurement Repeatability



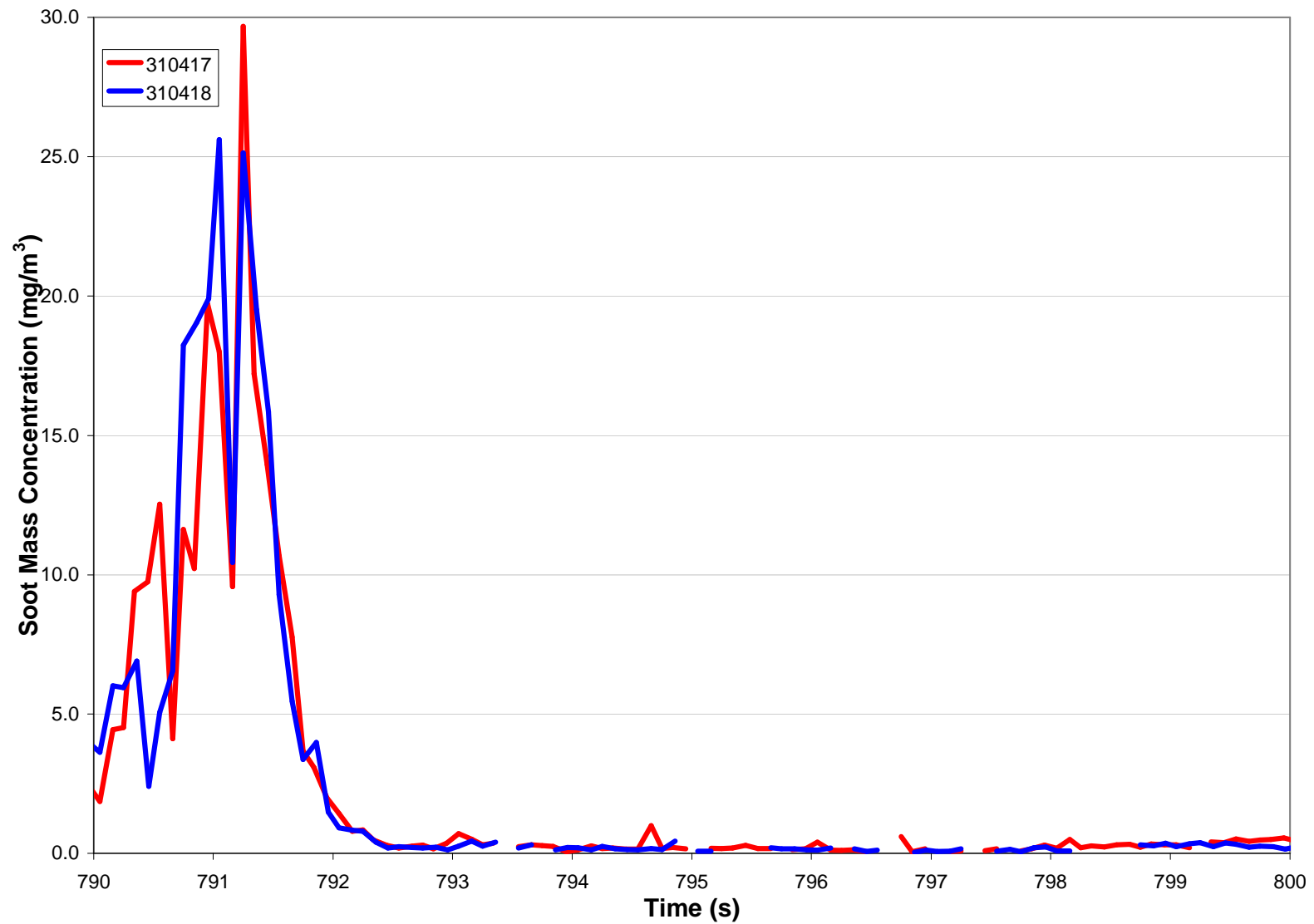
Section of Diesel FTP Cycle from **Dilution Tunnel**, 4 Repeats



Raw Exhaust (600-750s – 2 repeats)



Raw Exhaust (790-800s – 2 repeats)



LII Optics Subjected to Mil Spec Vibration Testing

MIL-STD-810F Method 516.5 – Shock



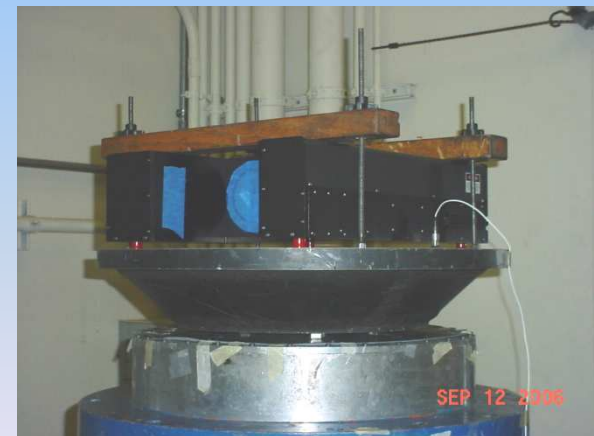
Preparation for On road and
Helicopter Flight Tests



X Axis



Y Axis



Z Axis

Applications – On-Road Measurements



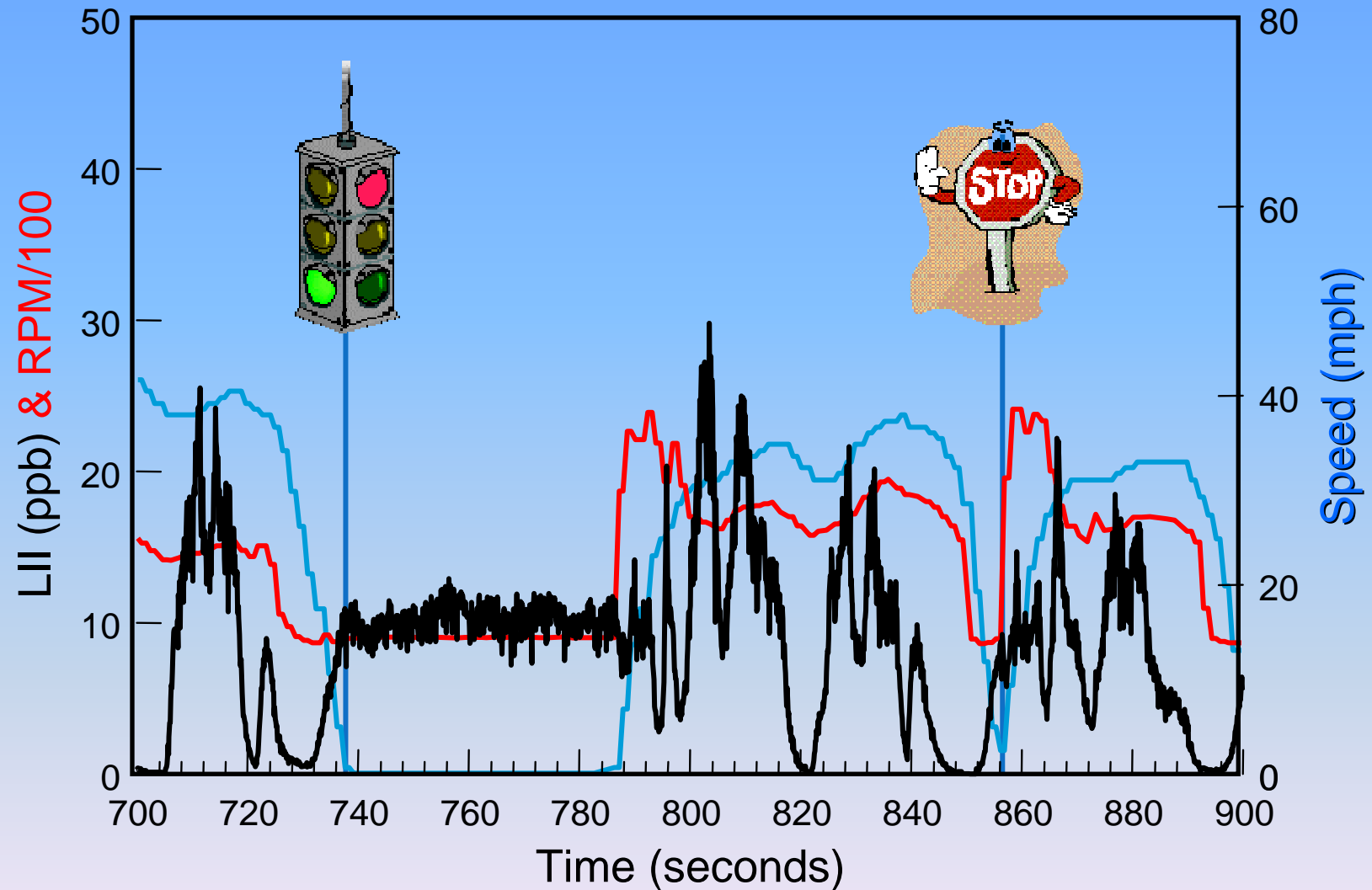
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Spray Diagnostics

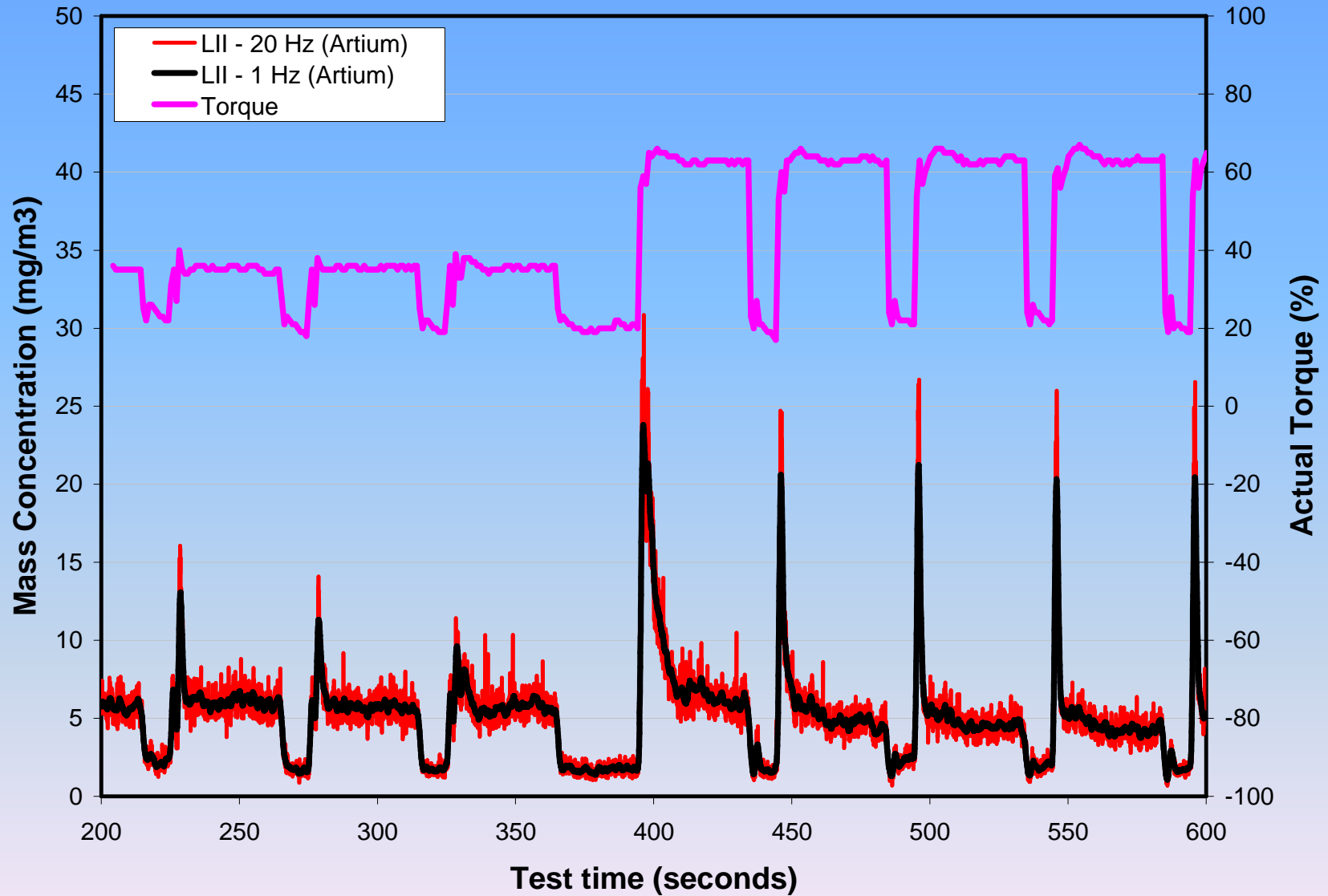
Particulate Emissions

Cloud Research

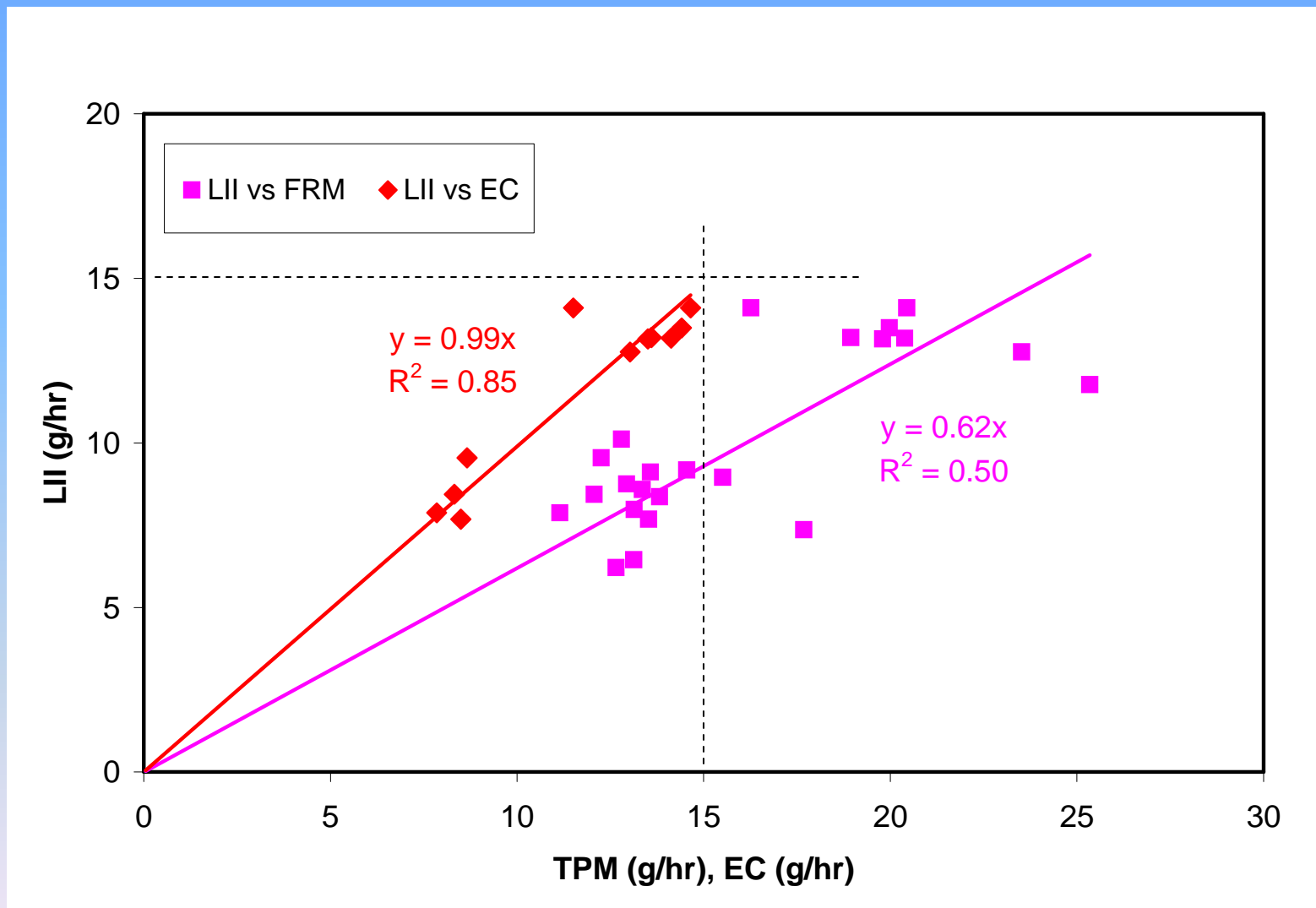
VW TDI: Stop-Start Urban Driving



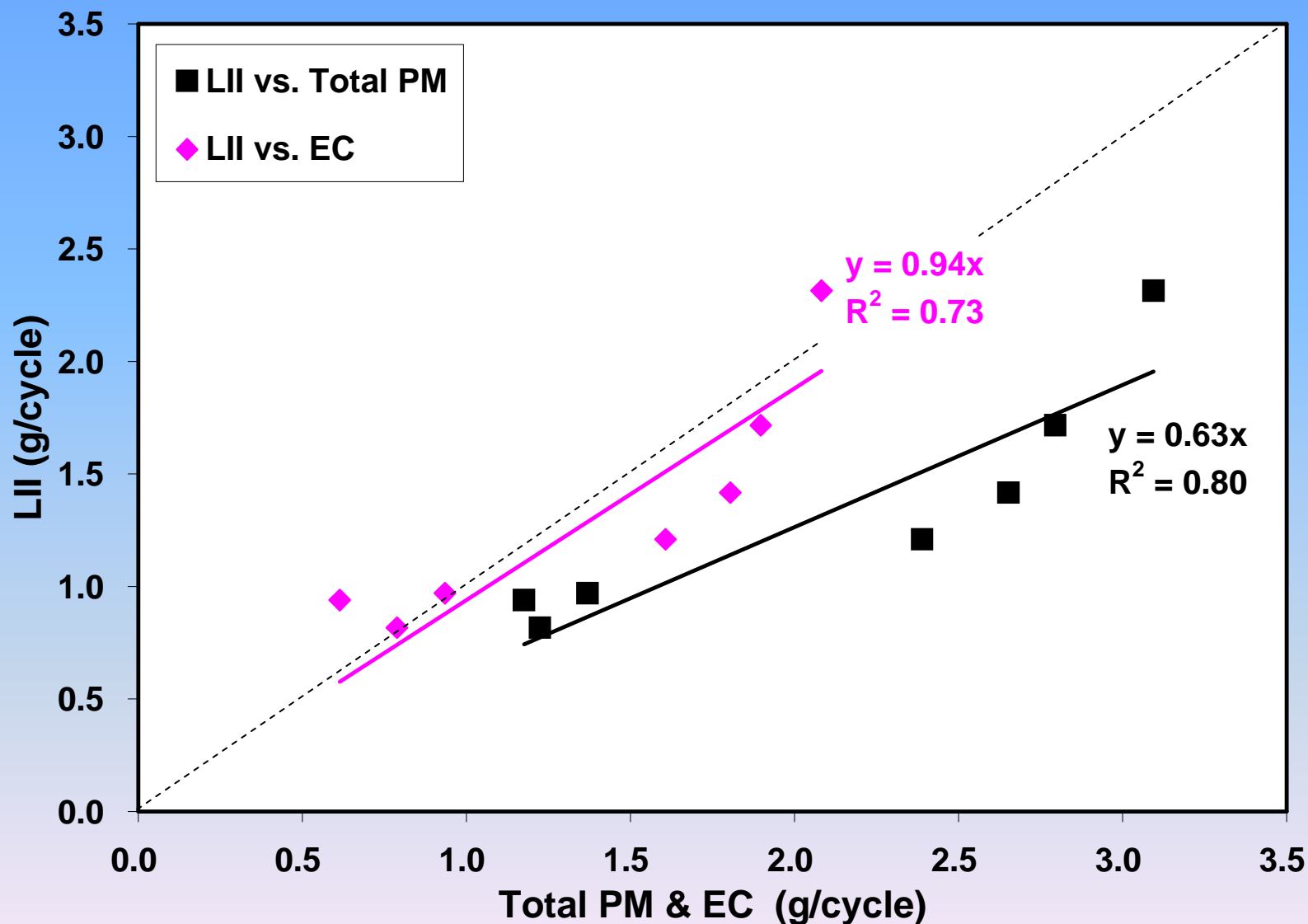
NTE Cycles with CARB



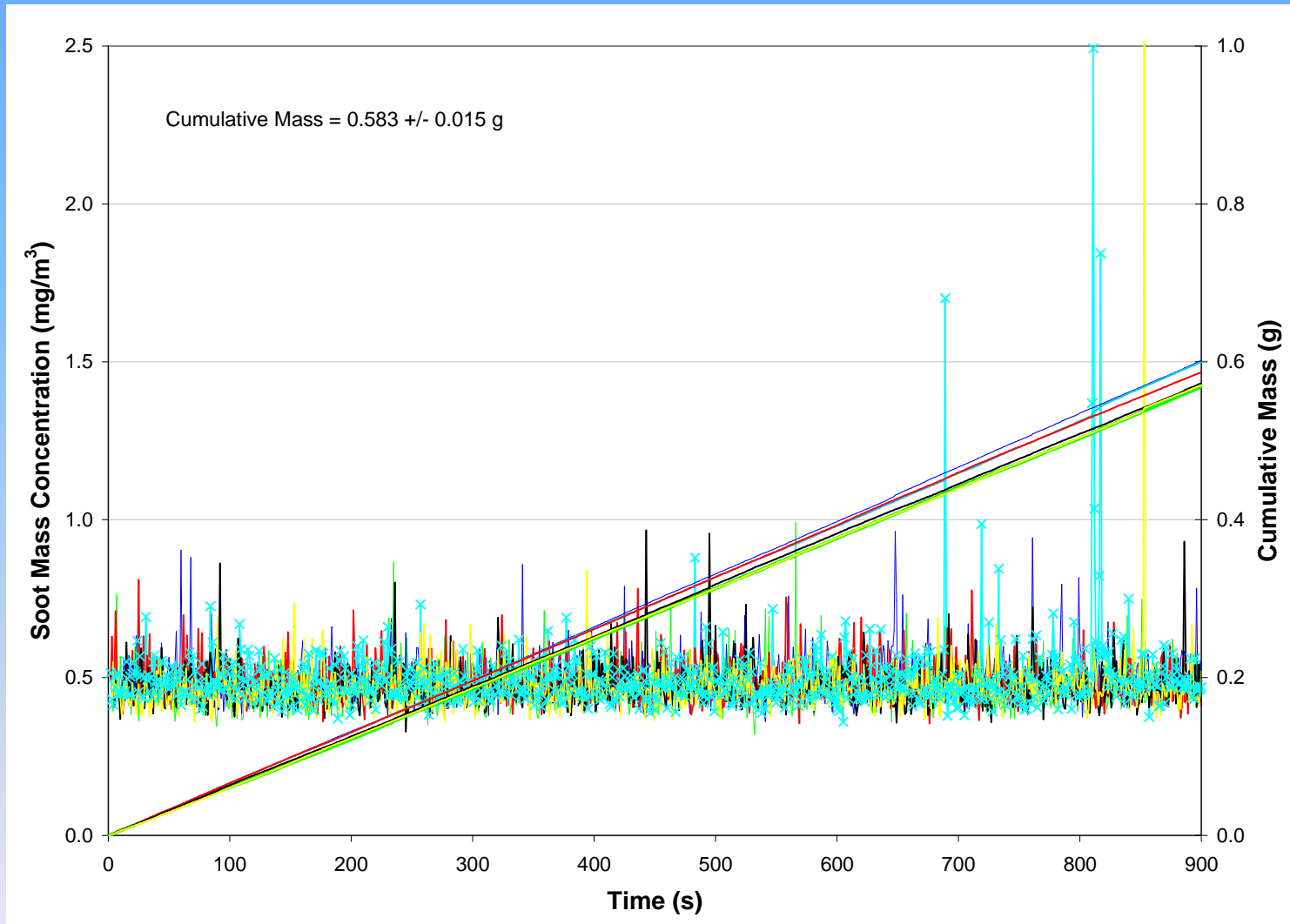
CARB: Heavy-Duty Diesel NTE Summary



CARB: Heavy-Duty Diesel On-Road Summary

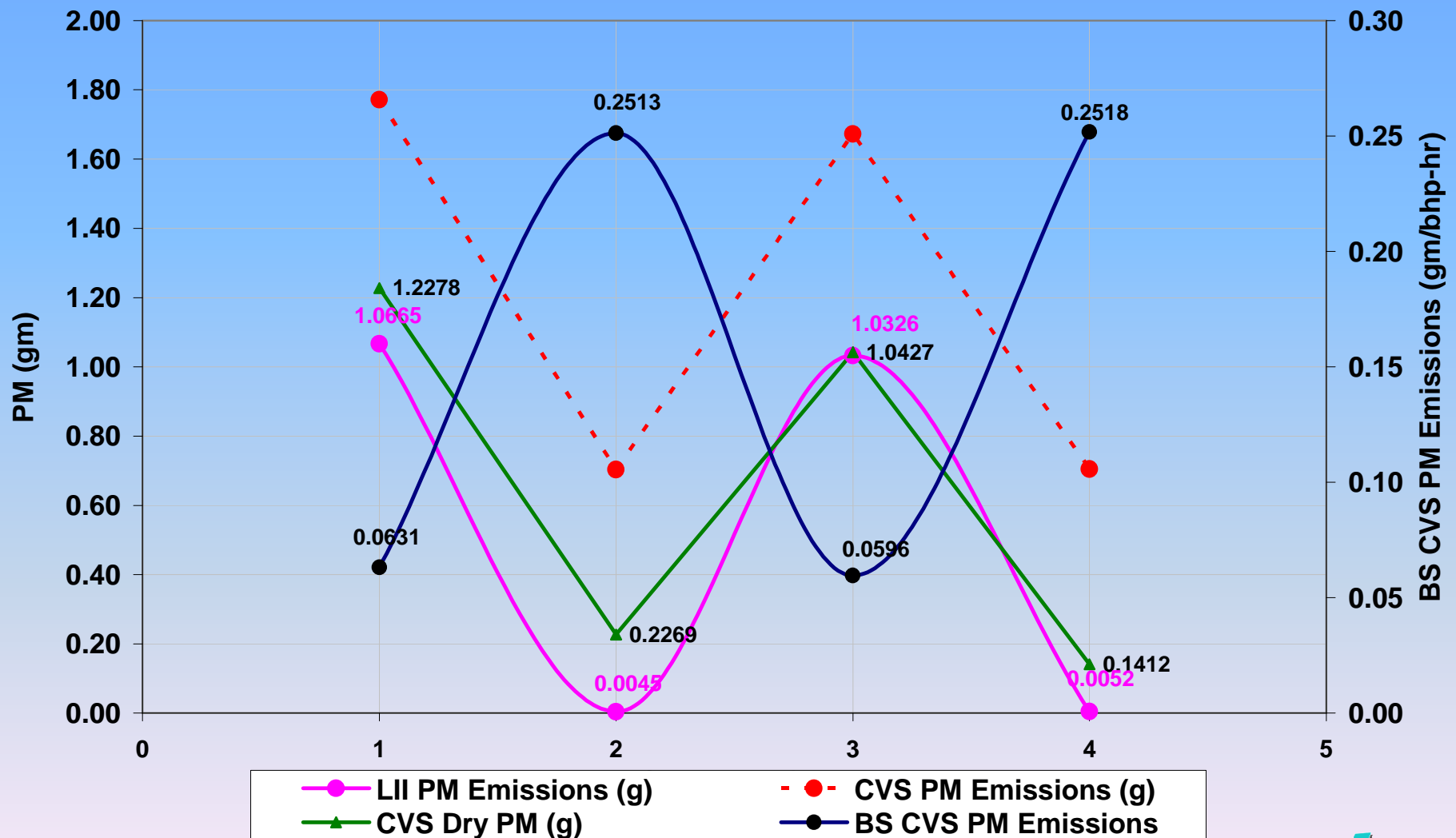


HDDM2 – Steady State – 6 Repeats



HDDM1 – Dilute Exhaust

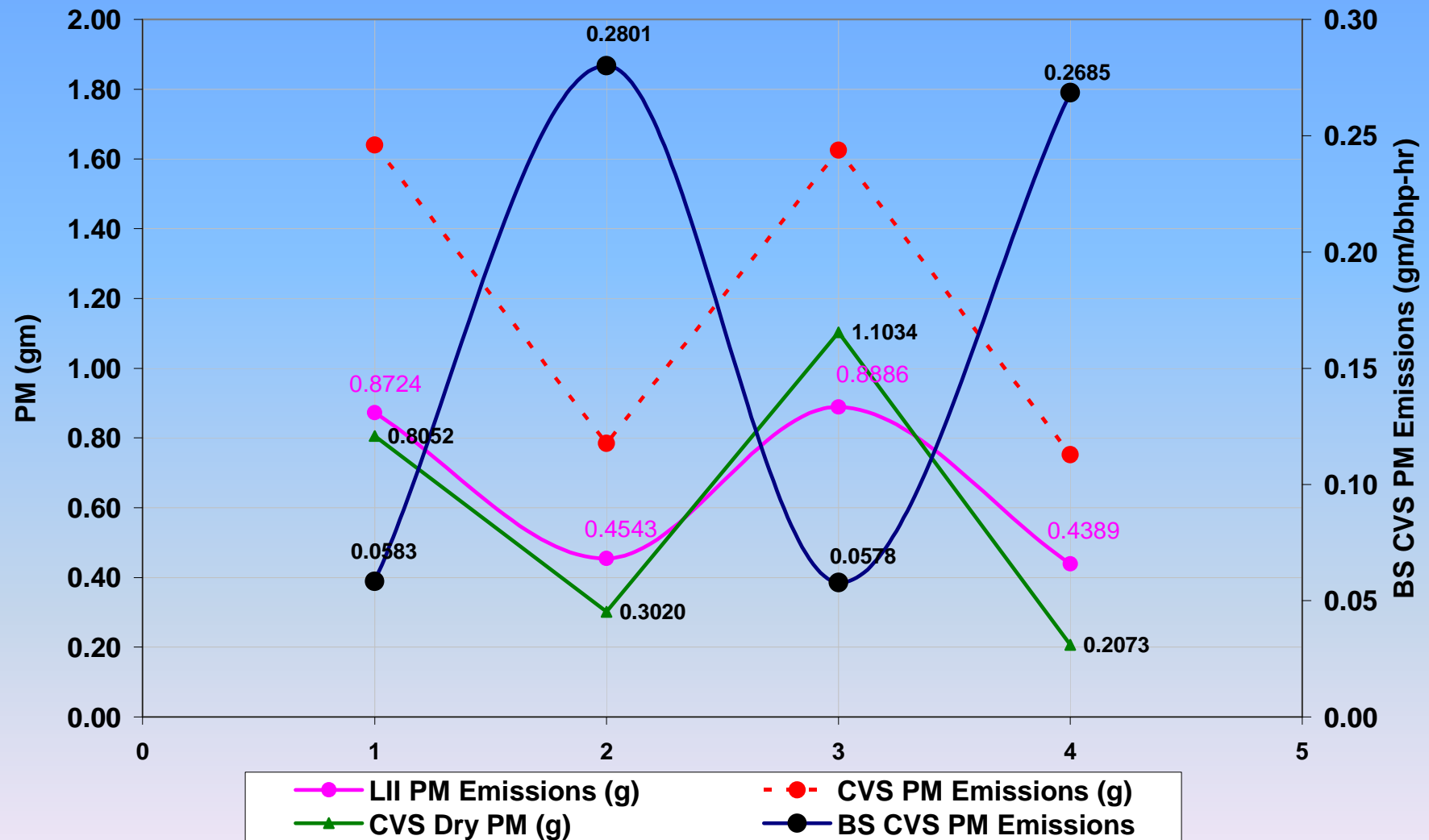
LII Sampling Dilute Exhaust



testing at Cummins

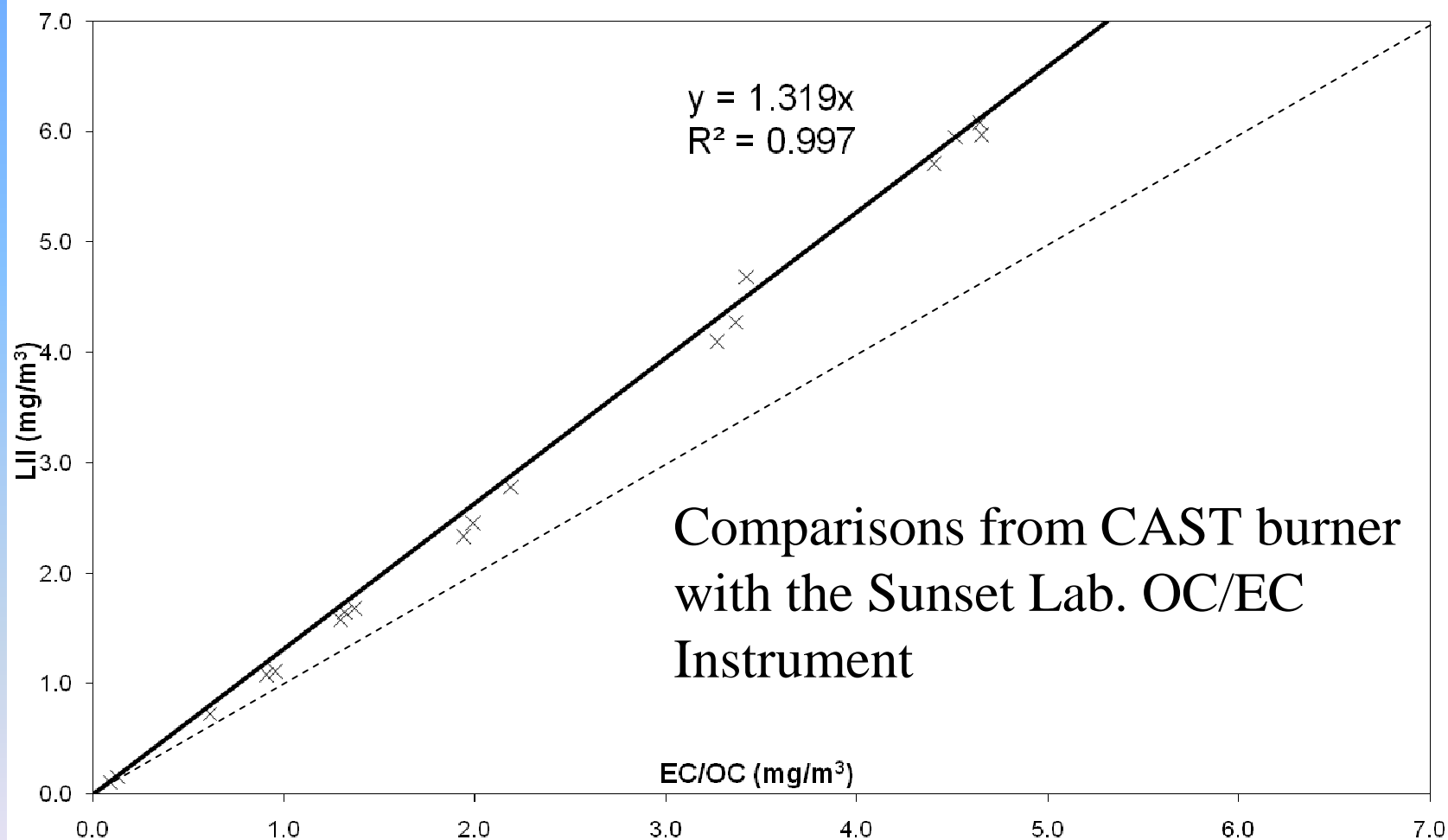
HDDM1 – Raw Exhaust

LII Sampling Raw Exhaust

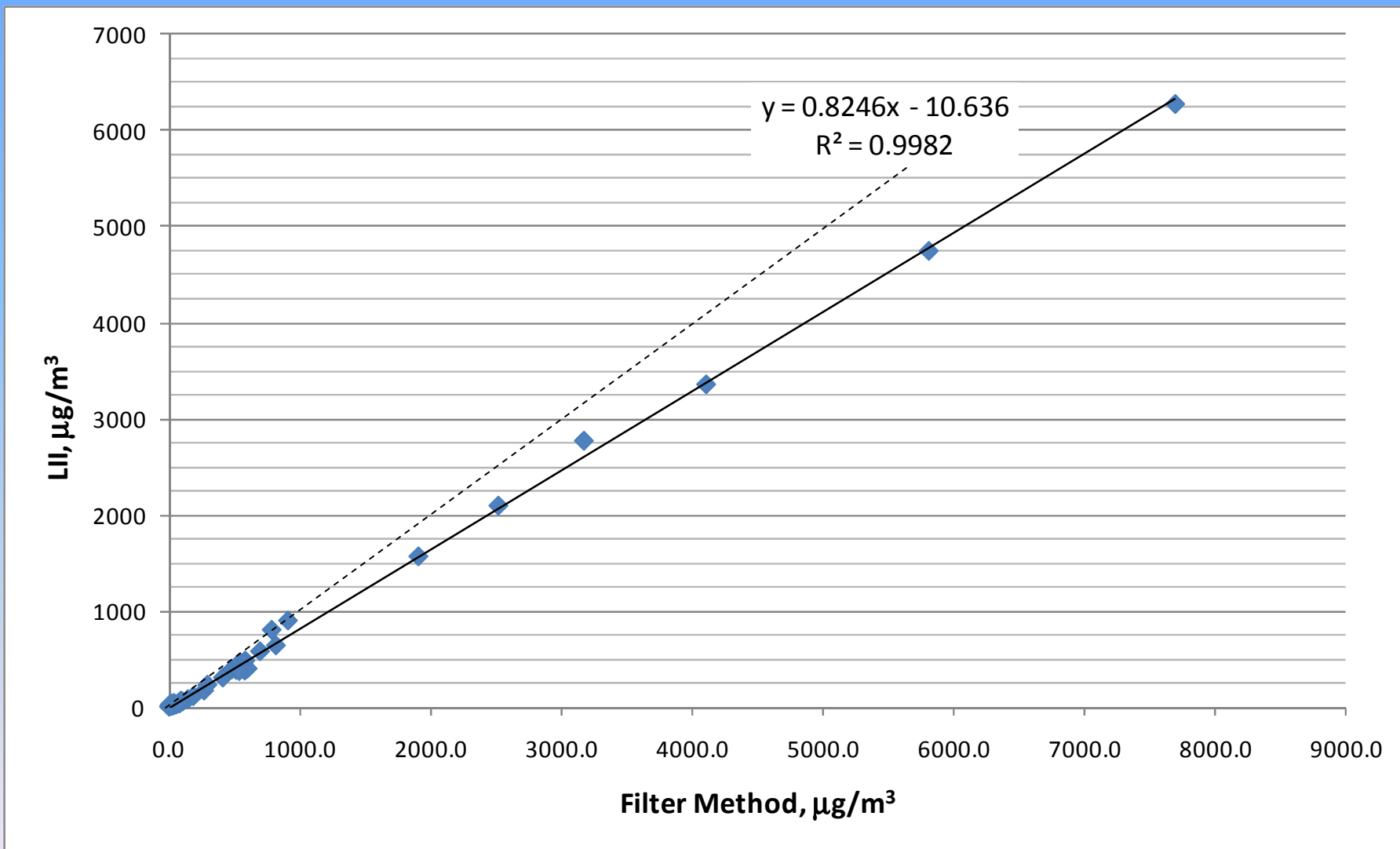


testing at Cummins

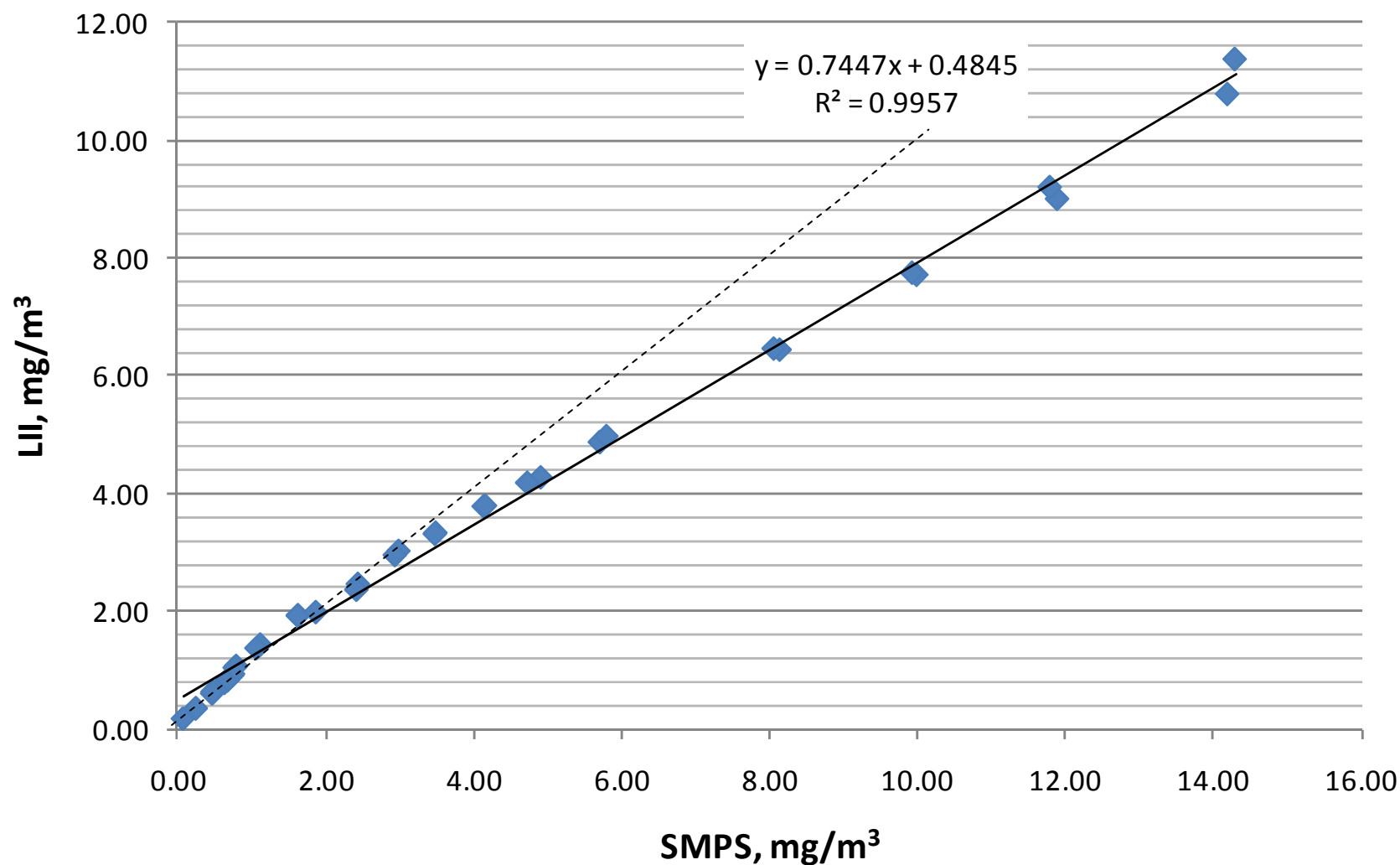
SwRI Instrument Comparisons



NASA Glenn Research Center tests conducted on soot from a mini-CAST burner in December 2009 prior to measuring gas turbine particulate emissions



NASA Glenn measurements of soot generated by the mini-CAST burner and compared to the TSI SMPS measurements.

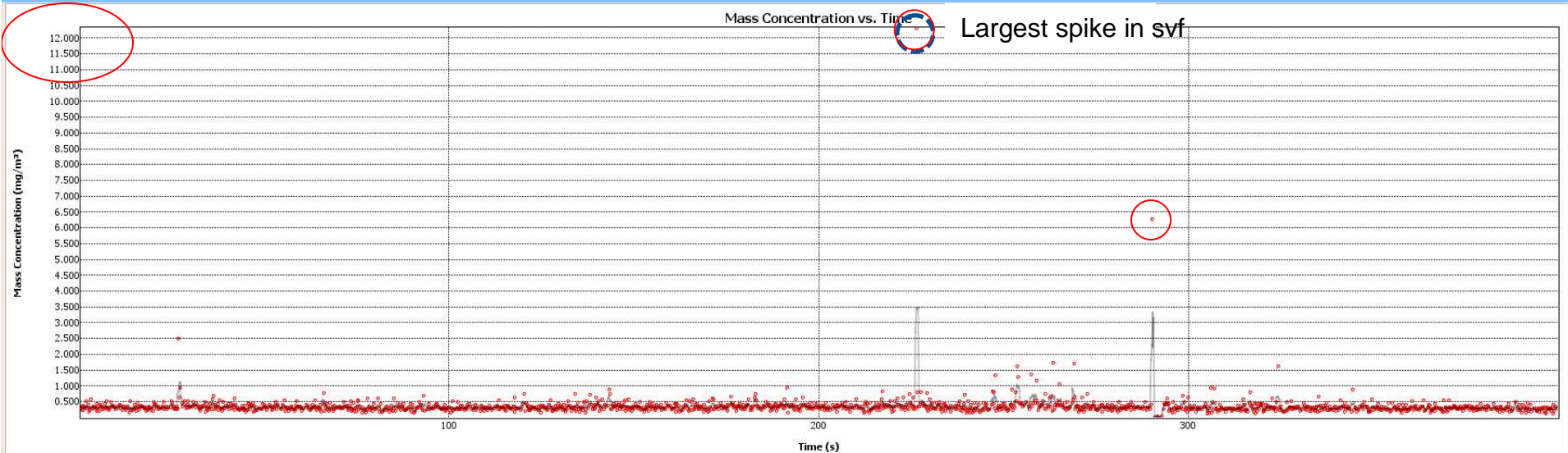


The Mystery of Inconsistent LII Measurements

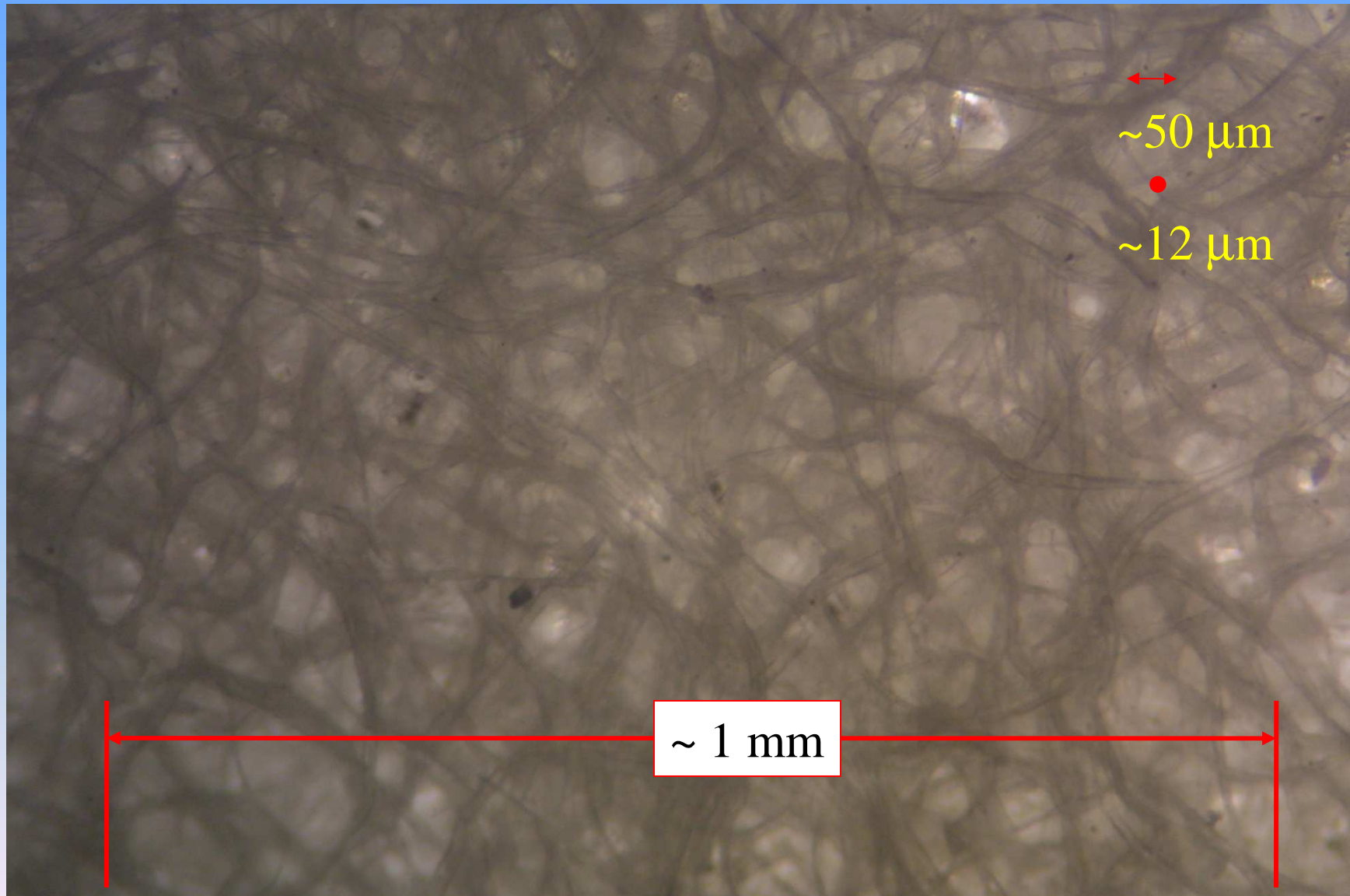
Observations:

- During some tests, LII showed variances from run to run
- Poor agreement with gravimetric
- Poor agreement with MAAP and other filter-based instruments
- Large spikes in time svf history

Observation: *SVF versus time plots show isolated spikes in the SVF values which cannot be accounted for as large concentrations of soot aggregates passing the sample volume. In the turbulent flow, such high concentration gradients do not exist for long.*



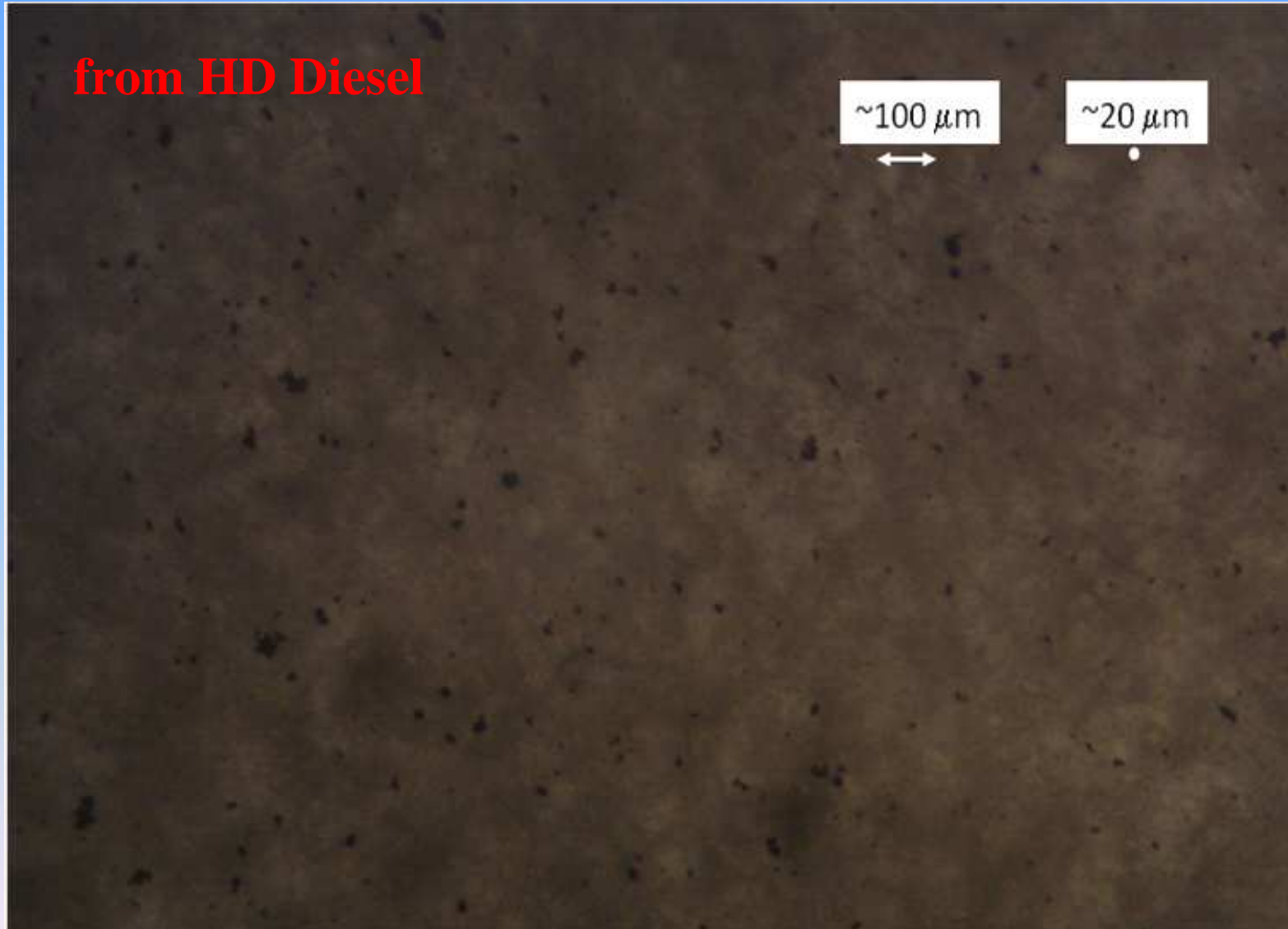
Photograph of the Filter under an Optical Microscope



Cardiff Tests 31-3-09 to 1-4-09

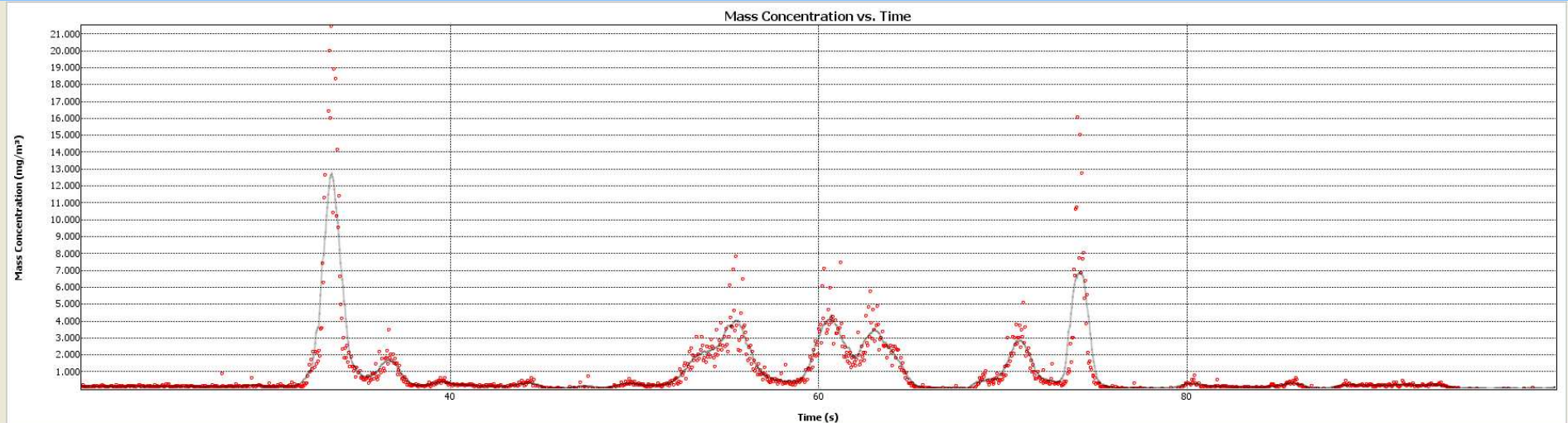
Sample contamination with large agglomerates of soot shed from sampling line surfaces

from HD Diesel



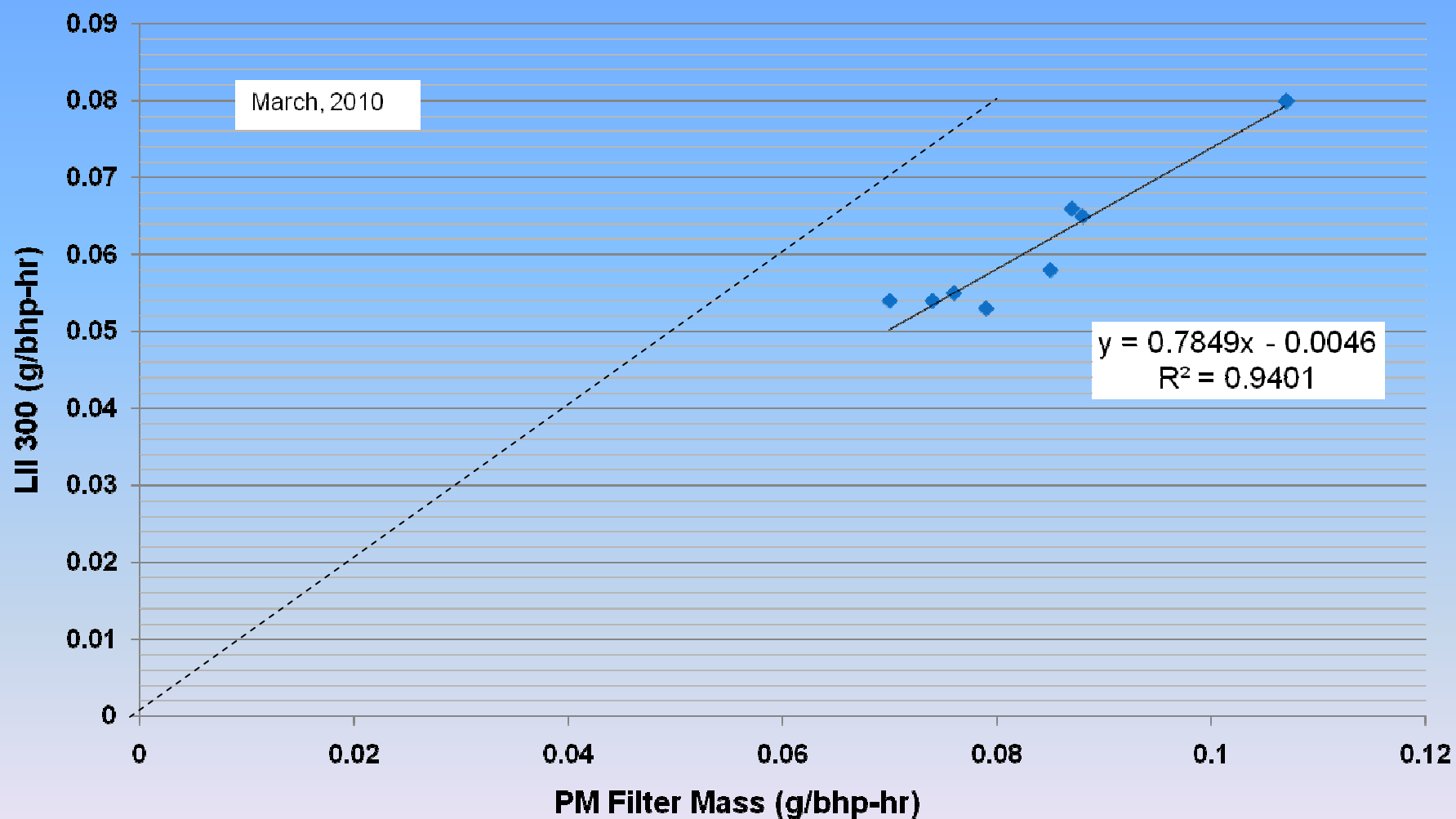
The Problem of Large Agglomerates

After cleaning the cyclone separator, a close observation of a section of the FTP cycle shows that the LII measurements consistently rise and fall shot to shot indicating that there are no individual spikes in the data. This implies that there are no large particles in the sample and so the results should agree with gravimetric.



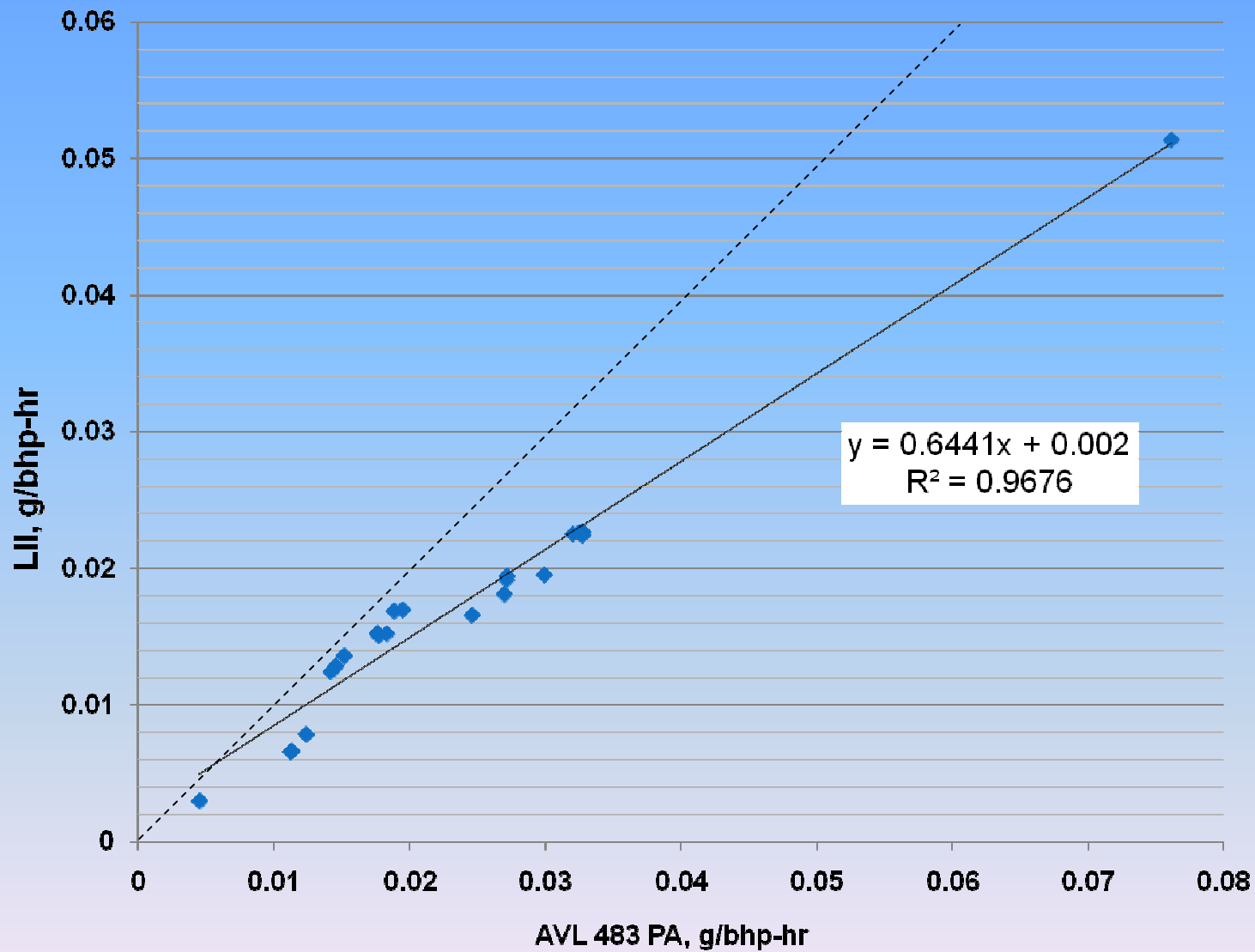
Recent Tests at Cummins

Comparisons of LII 300 and Gravimetric

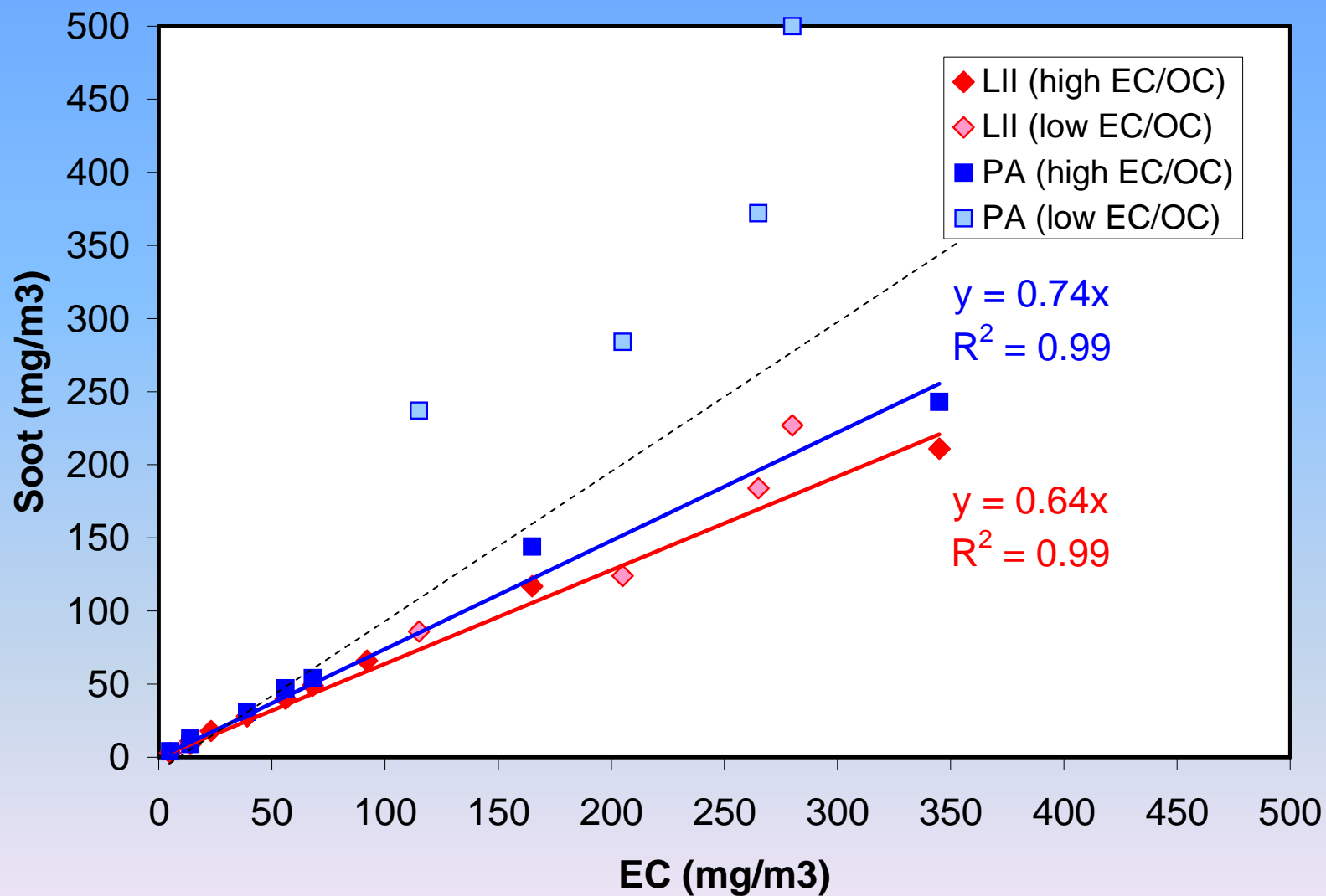


Cummins Instrument Comparisons

March 2010



Calibration Curve for Conventional LII-to-Mass



Field Tests at the Port of Oakland Shipping Yards





LII 300 Setup for Field Testing

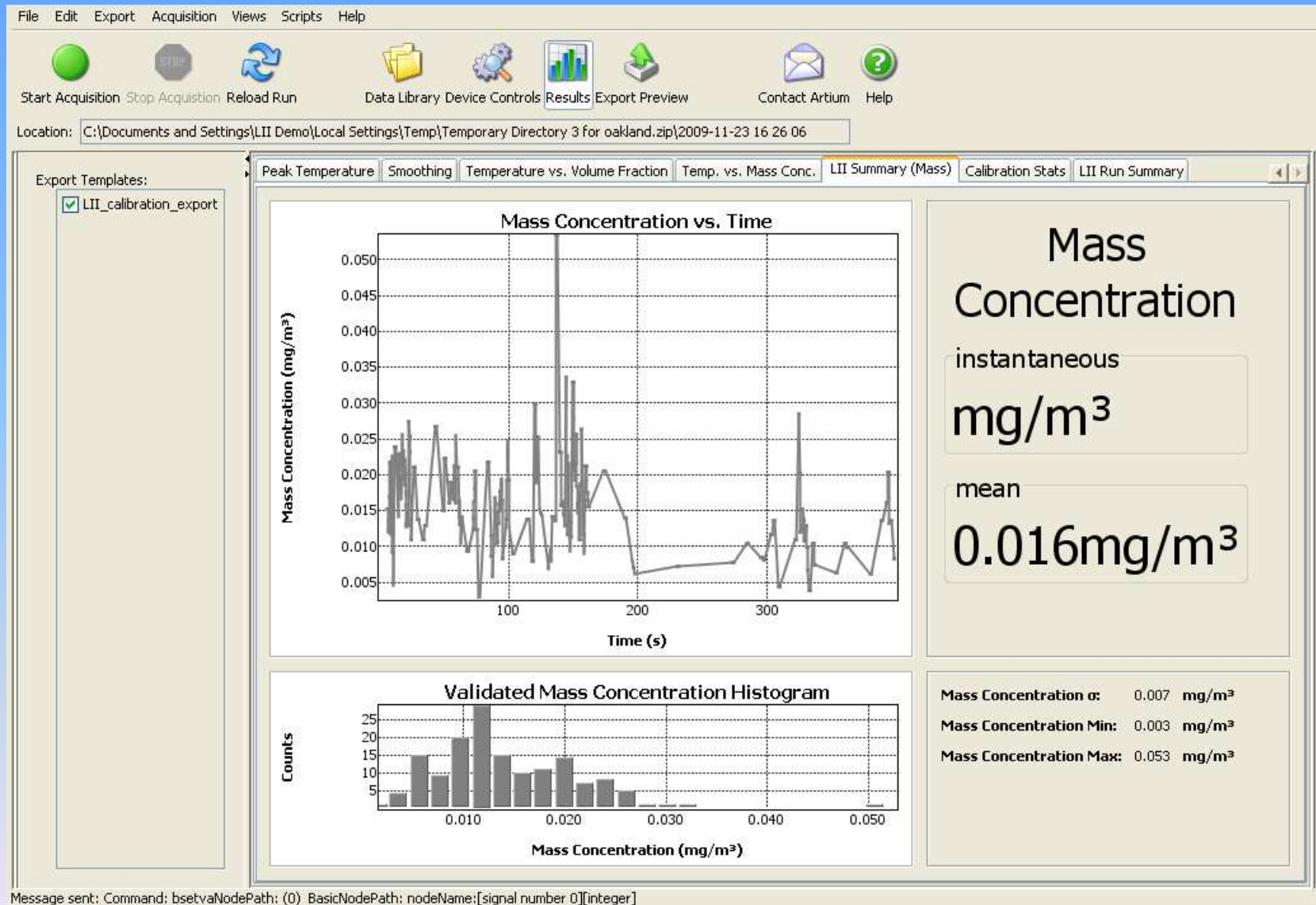
Test Location – Port of Oakland Overpass to Shipyards



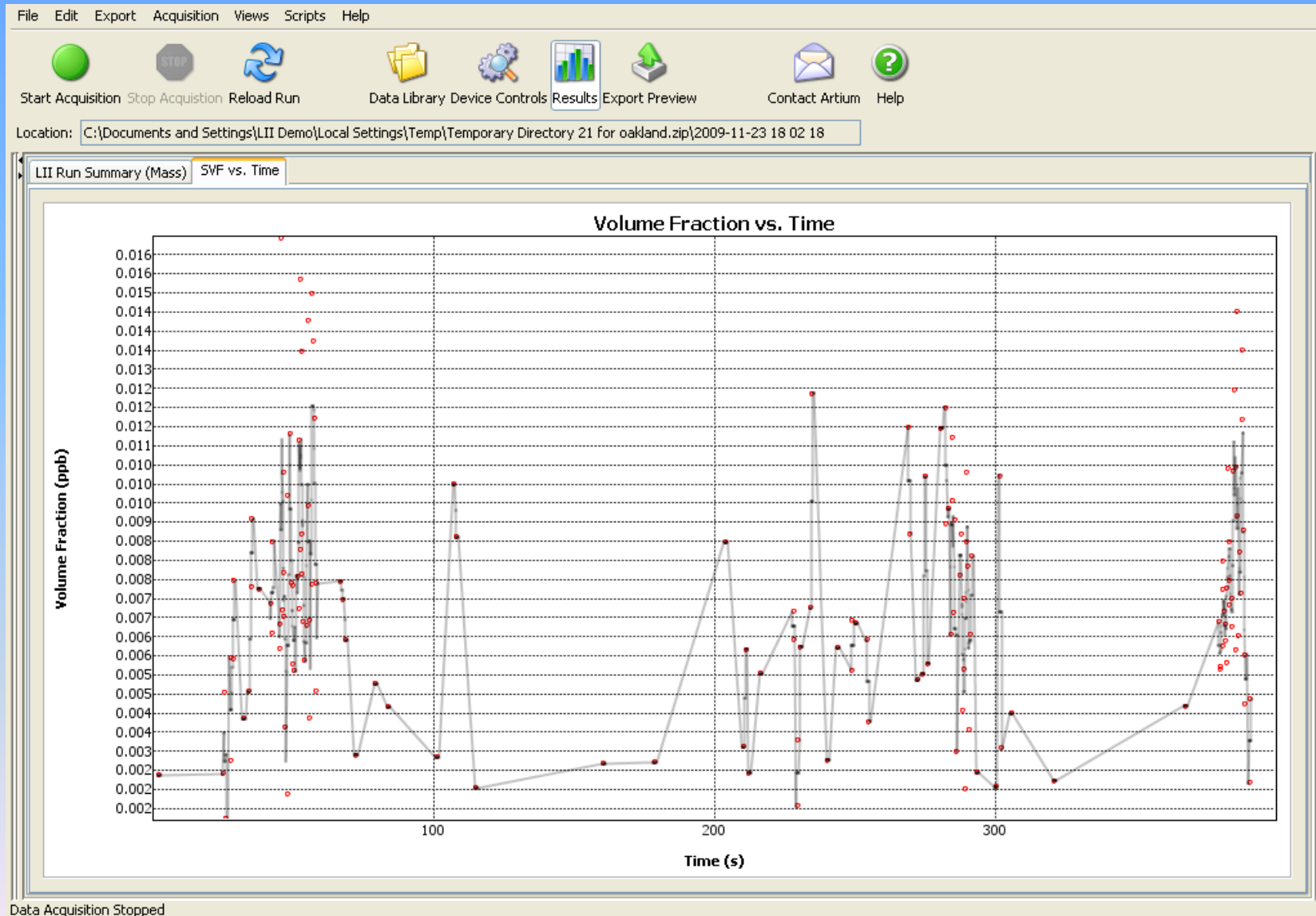
Atmospheric Sampling In Neighborhood of Port of Oakland



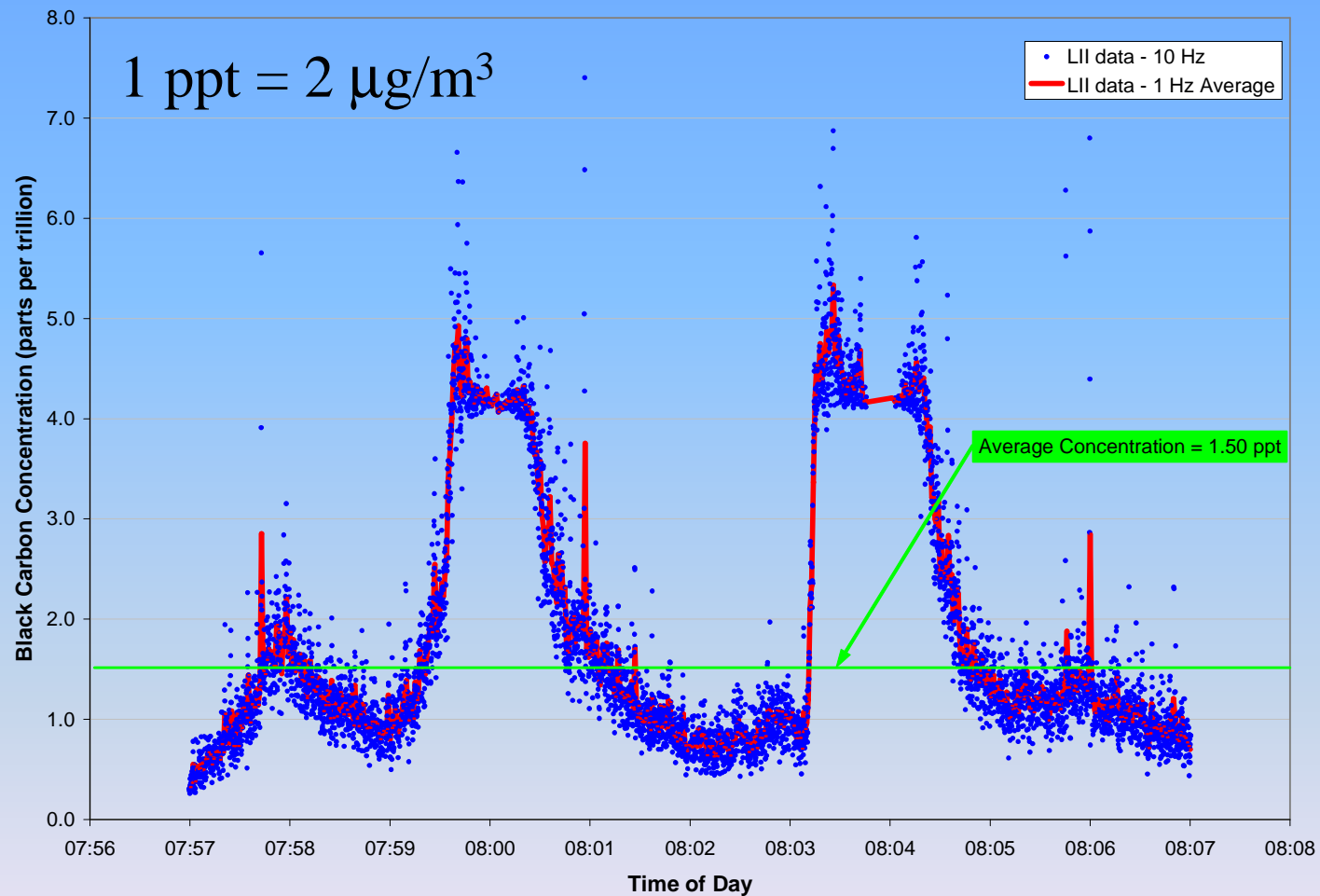
Sample Data From Oakland Shipyard Tests



Variation of Soot Volume Fraction with Time (truck transits)



NRC Canada Very High Sensitivity LII



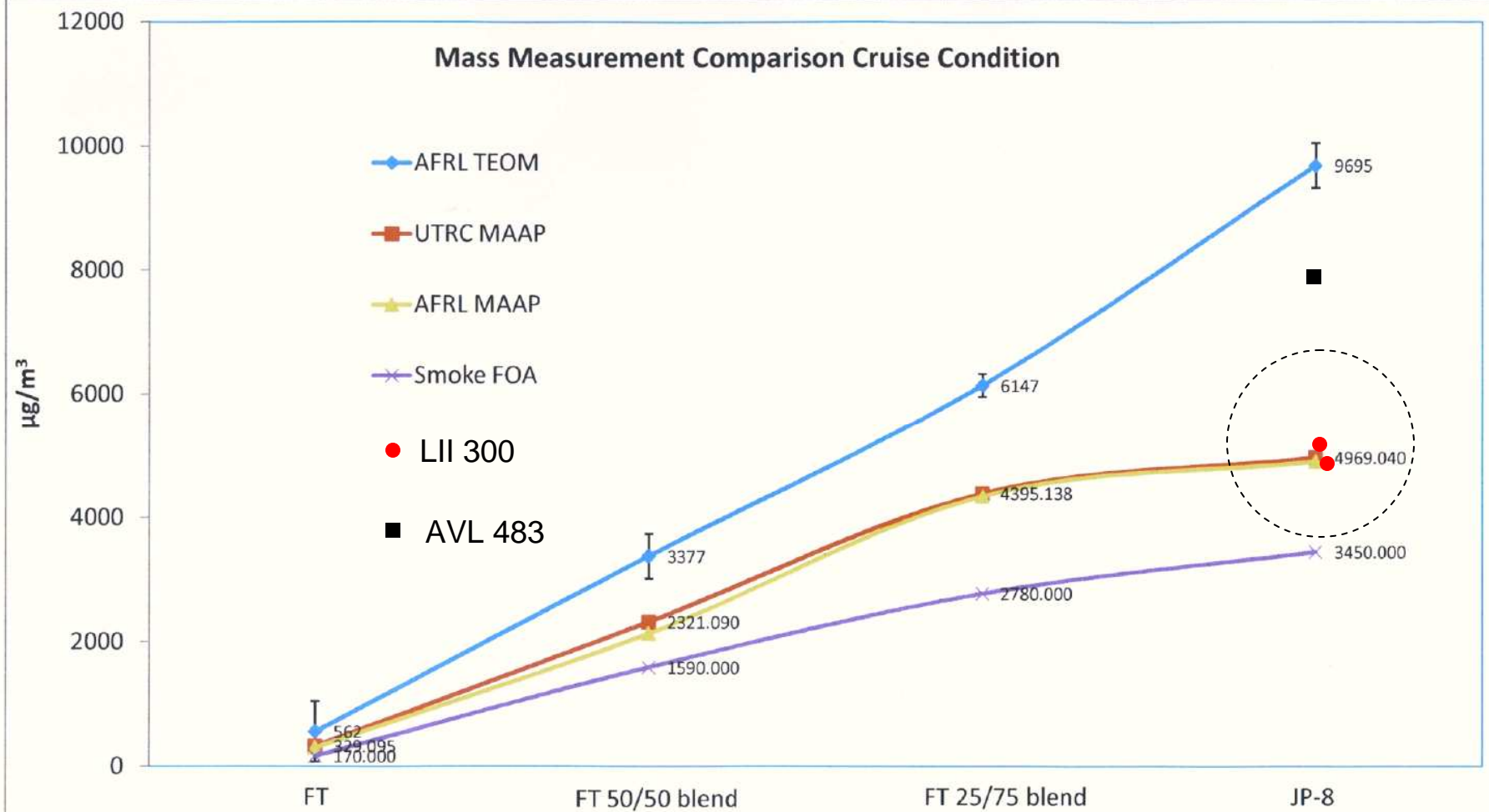
Turbine Engine (Helicopter) Tests at Wright Patterson AFB SAE E31



Turbine Engine (Helicopter) Tests at Wright Patterson AFB SAE E31



Data Acquired at Wright Patterson AFB (SAE E31)



Early Breadboard LII Instrument at NRC Canada

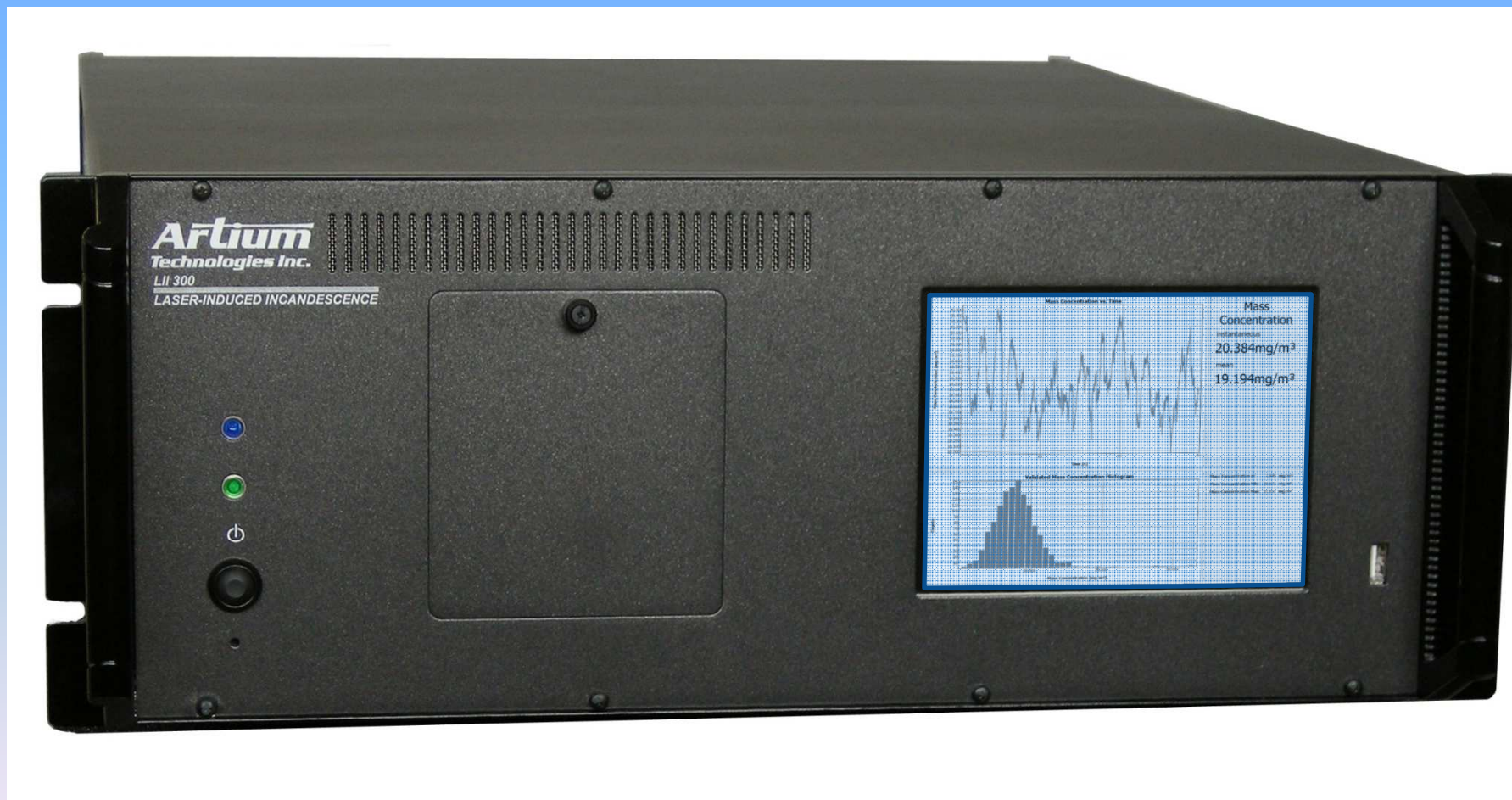


LII 200 Developed for Lab Use



LII 300 LASER-INDUCED INCANDESCENCE Instrument for Soot Characterization

Artium Technologies, Inc. provides the **LII 300** system, the most advanced laser-induced incandescence instrument available in the market today.



Measures Soot Concentration (mass or volume basis), Specific Surface Area, and Primary Particle Diameter in Real-Time

Artium
Technologies Inc.

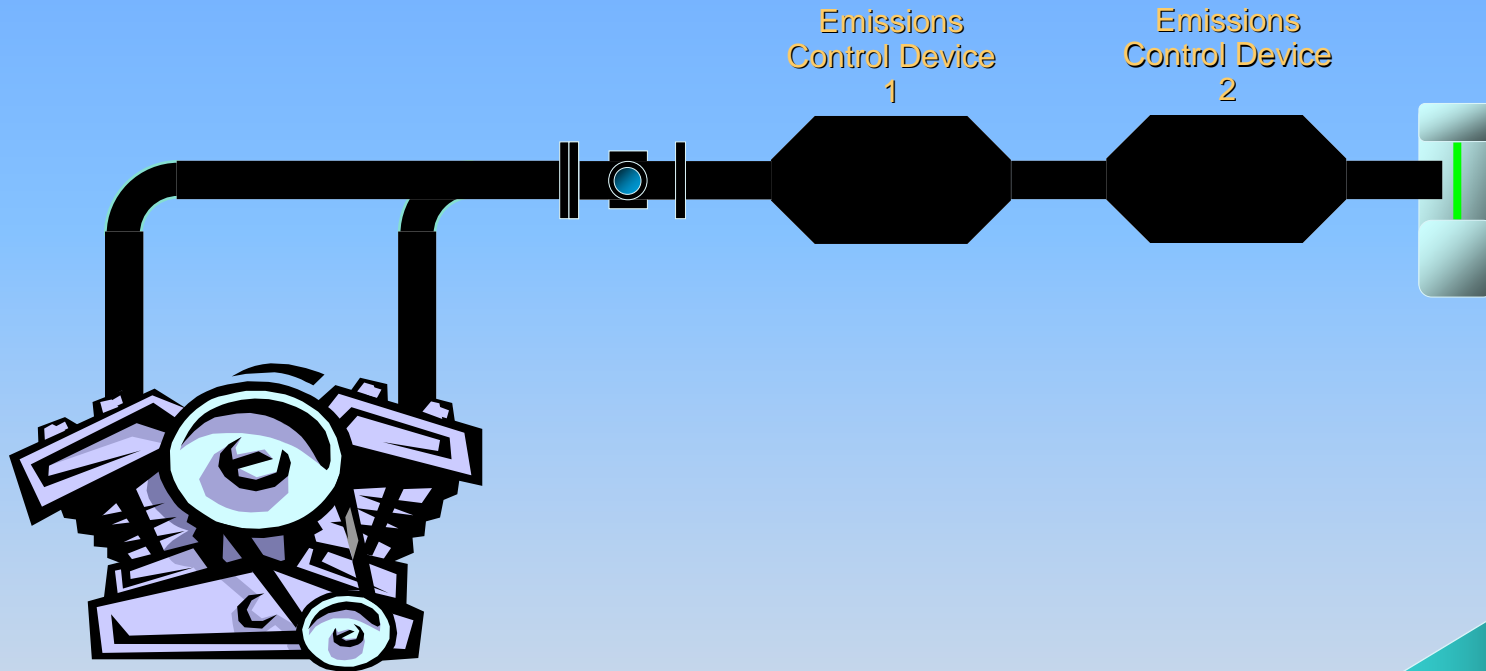
Summary: LII Features

- *in situ* and nonintrusive
- signal is proportional to soot volume fraction
- spatially resolved measurements
- time resolved
- large measurement range
 - not limited by aggregate size
- high precision and repeatability
- high speed data acquisition and analysis

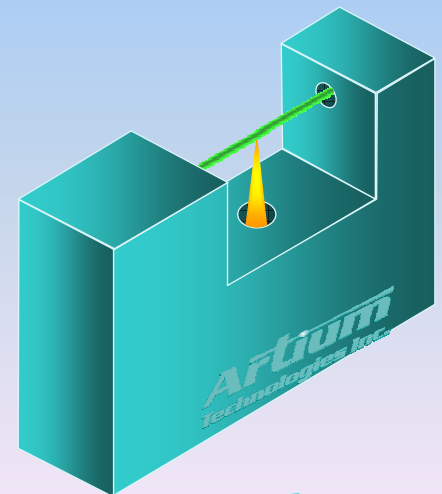
Summary LII Benefits:

- dilution of sample not required
- stable measurement of elemental carbon
- insensitive to presence of other species
- can operate at very low concentrations
- real-time results
- cycle-resolved measurements possible
- can provide particulate morphology (size, size distribution, number density) when combined with scattering

LII in Emissions Control Development



- LII provides sensitivity for post-2007 regulations (measures *microgram per cubic metre* concentration)
- Ideal for measuring engine-out / emissions-control-systems-in particulate levels
- Evaluate emissions control system efficiency



Artium
Technologies Inc.

LII Particulate Monitoring Instrument

Sealed enclosure

Sampling Hood

Develop, Evaluate, and Commercialize

Laser-Induced Incandescence (LII)

Systems for Online Exhaust Particulate Material (PM) Monitoring



Other Mobile PM Sources



Thanks for your attention!

Questions or Comments?

Thanks again for
Development Support by California Air Resources Board
Innovative Clean Air Technology (ICAT) Grant 06-03

Artium
Technologies Inc.

Spray Diagnostics

Particulate Emissions

Cloud Research